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Development of Two-dimensional Pollutant Transport Model for Response of Toxic Chemical Spills in Rivers

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Abstract of Dissertation

Development of Two-Dimensional Pollutant Transport Model for the Response of Toxic Chemical Spills in Rivers

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The pollutant spill accidents in rivers more frequently occur since the high-tech industries are growing up in recent years. The accident can lead direct damages to human society such as contaminating drinking water and irrigation water. In Korea, the damage will be more significant since 90% of quantity of water intake is from surface waters. Therefore, response measures are needed to respond to pollutant spills in rivers.

Some accidents, however, cannot be treated by direct measures such as chemical treatment and blocking the river water. Therefore, it is necessary to cope with passive countermeasures by expecting the spatiotemporal distribution of the pollutants. Ministry of Environment has operated 2 type of response systems for it. One of them is developed for the 4 main rivers, and another is developed for tributaries of 4 main rivers. Nonetheless, those systems were appraised as difficult to operate since they adopted

foreign water quality model. In this study, two-dimensional pollutant transport model for response, which is called CTM-2DT, was developed based on FEM, and an algorithm for identifying the significant reaction was proposed.

CTM-2DT is a toxicant analysis version of CTM-2D which is two-dimensional water quality model developed by Seoul National University. CTM-2DT can represent mechanisms of volatilization, adsorption/desorption, and biochemical reactions. Each reaction mechanisms were expressed as first reaction terms, so each term requires an equilibrium concentration and rate of change. Additionally, parameter estimation equations of each terms were installed so that the parameters be obtained through database in order to prepare for the accident immediately. In order to verify the constructed reaction terms, the results of the analytical solution and the model were compared. The error was less than 0.1%, which proved the validity of the model.

An algorithm for identifying significant reaction terms was proposed in order to operate the developed model efficiently. The algorithm process is as follows: (1) figuring out the hydro-conditions and topography from hydrodynamic model results, (2) constructing virtual rectangle channel based on the conditions in step 1, (3) performing one-at-a-time sensitivity analysis for each parameters of reaction terms to find critical parameter values, and (4) examining the significant reaction by comparing the critical values and target material properties, (5) conducting simulation with only significant reaction mechanisms so that the calculation time can be reduced.

The developed model and algorithm were applied to assess validity of the algorithm. The virtual accident was assumed as the toxic chemical inflows into the Kumho River where joins the Nakdong River. It was assumed that methyl chloride is assumed to be introduced at Jugok drainage station, accordingly concentration-related-data were figured out at Hwawon intake station located in the downstream. The riverbed elevation referred to the survey data in 2016 by Advanced Research Center for River

Operation and Management (ARCROM). And the hydraulic data referred to the National Water Resources Management Integrated Information System (WAMIS).

In order to examine applicability, three cases were compared taking into account the significant mechanism mentioned above ((1) results reflecting all reaction terms, (2) results reflecting only significant mechanisms, (3) results without reactions). In case of methyl chloride, the volatilization and biochemical reactions were identified as significant mechanisms while the sorption process was not. When comparing the case 2 and 3, the residence time at the Hwawon intake station was about 33% with about 2 hours difference. Also, in case of the peak concentration, there was 100% difference. When comparing the case 1 and 2, there was 3% changes in peak concentration and residual time which can be regarded as an acceptable difference considering the need for conservative judgment. The results showed that the algorithm for identifying significant reaction is valid in the given condition. Moreover, the calculation of case2 took only 1/4 times compared to case 1, and it is expected to provide a more appropriate countermeasure for the accidents.

Therefore, it is expected that the pollutant transport model for toxic chemicals and the algorithm for identifying the significant reaction mechanism in this study help to provide quicker decision for response to the river spill accidents.

Keywords: river spill accident, accident response system, 2D numerical model, toxicant transport model, significant reaction mechanisms.

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Latin uppercase

C = Concentration [$\mathrm{kg/m^3}$]

C_d = Mass dissolved in water per volume of water [$\mathrm{kg/m^3}$]

C_p = Particulate mass adsorbed to suspended sediment per volume of water [$\mathrm{kg/m^3}$]

C_s = Mass of suspended sediment per volume of water [$\mathrm{kg/m^3}$]

C_{pb} = Particulate mass adsorbed to riverbed per volume of water [$\mathrm{kg/m^3}$]

C_r = Concentration of contaminants in porous particles [$\mathrm{kg/m^3}$]

C_{eq} = Equilibrium concentration [$\mathrm{kg/m^3}$]

D = Diffusion coefficient [$\mathrm{m^2}/s$]

D_{aq} = Aqueous diffusion coefficient [$\mathrm{m^2}/s$]

D_{50} = Median diameter of sediment [m]

D_b = Deposition velocity [m/s]

$\mathrm{E_b}$ = Erosion velocity [m/s]

$\bar{H}$ = Average water depth [m]

K_P = Partitioning coefficient between soil and water [$\mathrm{m^3/kg}$]

K_{oc} = Partitioning coefficient between organic carbon and water [$\mathrm{m^3/kg}$]

K_{ow} = Partitioning coefficient between octanol and water [$\mathrm{m^3/kg}$]

W_s = Settling velocity of sediment [m/s]

Latin lowercase

f_{oc} = Fraction of organic carbon in soils [-]

h = Water depth [m]

k_s = Exchange rate of sorption process [1/h]

k_r = Reaeration coefficient [1/day]

k_v = Volatilization coefficient [1/h]

r = Radial distance [m]

t = Time

Greek lowercase

α, β = Regression coefficient [-]

δ_m = Thickness of mixing layer [m]

ρ_b = Bulk density of riverbed ($=\rho_s(1-\phi)$) [kg/m^3]

ρ_s = Particle density of sediment [kg/m^3]

ϕ = Porosity of riverbed [-]

λ = biochemical reaction coefficient [1/h]

1. Introduction

1.1 Research background and necessity

Many rivers through the cities are prone to pollutant spill since the new materials are frequently used with the growth of the advanced industries. The number of the river spill accidents has recently increased. As shown in **Figure 1.1**, the accidents were constantly occurred in Korea: phenol spill into Nakdong River in 1991 at Gumi; Organic solvent spill into Nakdong River in 1994; phenol spill into Nakdong River in 2008 at Gimcheon; sulfuric acid spills in 2014 at Nakdong River and in 2017 at Osipcheon, and **Table 1.1** shows the lists. Especially, 90% of the domestic water supplies are from surface water, so the accident could affects their water uses directly. Accordingly, it is necessary to establish appropriate response measure for the river spill accidents.

The response measures are made according to the type of the accidents. In the case of small rivers or small amount of pollutant spill, direct response can be conducted through physicochemical measures such as chemical treatment and turning the river water. On the other hand, the accidents which are occurred in large rivers cannot be treated by the direct methods. In this case, it is necessary to cope with passive countermeasures by expecting the spatiotemporal distribution of the pollutants. Since the response measures are different by each accident as such, it is necessary to establish systematical procedures to respond to the accidents.

Various accident response systems have been developed such as Rhine Alarm

Table 1.1 Examples of pollutant spill accidents into river in Korea

Year	Pollutant	Location
1991	Phenol	Nakdong River (Gumi)
1994	Organic solvent	Nakdong River (Dalsung)
2008	Phenol	Nakdong River (Gimcheon)
2008	Oil	Nakdong River (Dalsung)
2014	Sulfuric acid	Nakdong River (Bonghwa)
2017	Sulfuric acid	Osipsheon

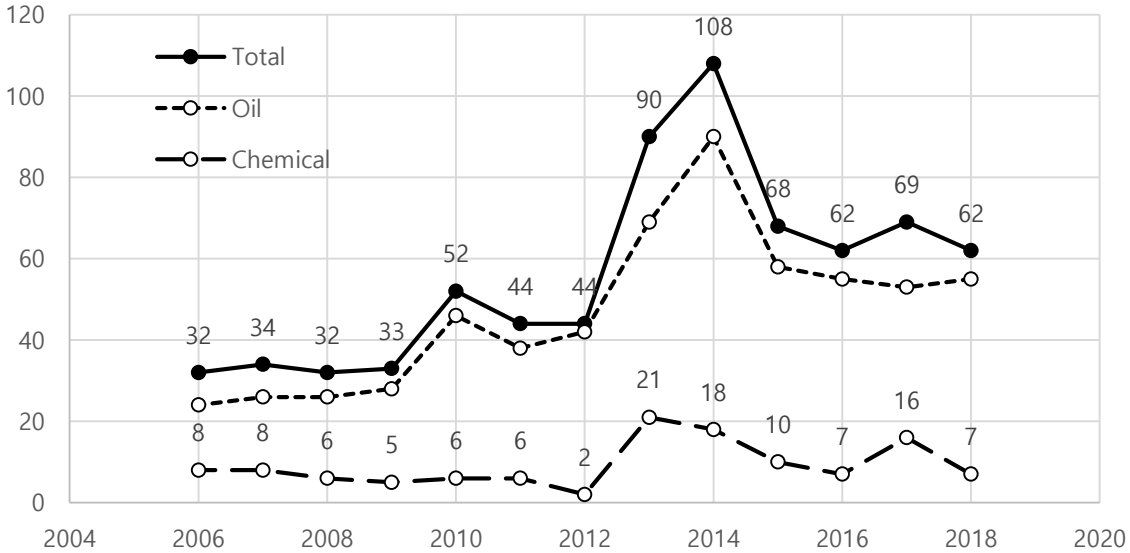


Figure 1.1 Statistics of Surface water pollution accident in Korea

Model (Griffioen, 1989) of ICPR (International Commission for the Protection of the Rhine), ICWater (Samuels et al., 2005) of EPA (Environmental Protection Agency), Water pollution Accident Response Management System, which is called as WARMS, (Mun et al., 2012) of NIER (National Institute of Environmental Research) etc., and those features are summarized in **Table 1.2**. These systems include contaminant transport model to predict the pollutants transport. The models can provide spatiotemporal distribution of the pollutants. In other words, it can support decision makers to prepare the accidents with the detail response strategy by quantitative analysis such as arriving time, retention time, and peak concentration. Considering these features of contaminant transport model, it can be one of the key parts of the system.

In Korea, Ministry of Environment has operated response systems for river spill accident as shown in Figure 1.2 which is the procedure of. Nonetheless, they has been evaluated that there are some limitations in maintenance and securing input parameters of pollutants. It is because the systems adopted foreign commercial software. Especially, WARMS which was developed for the 4 main rivers, adopted EFDC (Environmental Fluid Dynamics Code), EFDC is a multifunctional surface water modeling system, which includes hydrodynamic, sediment-contaminant, and eutrophication components (Tetra Tech., 2007). However this model reflects the isotropic dispersion coefficient which is not proper to domestic tributaries-rivers, and it is used as 2D model in the system, although it was developed as a quasi-3D model. Thus, this study focused on the development of 2D contaminant transport model for toxic chemical in rivers.

When the river spill accident occurs, it is important to respond to the accidents quickly. Accordingly, WARMS is operated to forecast spatiotemporal distribution of

Table 1.2 Representative response system for pollutant spill accident in rivers

Name	Institute	Dimension	Features
RiverSpill	NIER, Korea	1D	GIS-based accident response system for the tributaries using the analytic solution of 1D advection-dispersion equation.
WARMS (Water Pollution Accident Rseponse Management System)		2D	For four major rivers using EFDC-NIER, a modified version of EFDC certified by the US Environmental Protection Agency, as a water quality analysis model. However, it was assessed that there are limitations on the acquisition of input parameters of pollutants since EFDC is a model developed for estuaries and is not a self-developed model.
ICWater	Leidos, US	1D	GIS-based accident response system USEPA used it to response river pollutant spill due to the fire and terrors
RAM (Rhine Alarm Model)	ICPR, Europe (International Commission for the Protection of the Rhine)	1D/2D	Based on 2D water quality model which just reflects the simple mechanism of pollutant without volatilization and sorption processes.

pollutant in a timely manner using its automatic update of hydro module. In the system, however, all reaction mechanisms are considered when the simulation is performed, so unnecessary time is taken to calculate the insignificant mechanisms. Therefore, this study proposed an algorithm to identify the significant reaction mechanisms in the developed contaminant transport model.

1.2 Objectives and methodology

The main objective of this study is to develop the depth-averaged 2D numerical model to analyze the transport of the toxic chemicals accidentally spilled into natural rivers. To achieve this, the study focuses on the twofold as given below, and it is summarized in **Figure 1.2**.

Objectives 1. Construction of the two-dimensional toxicant transport model:

Objectives 2. Algorithm to identify the significant reaction mechanisms

For the first stage, this study focused on the development of the water quality model for the accident response system. The model basically solves the depth-averaged two-dimensional advection dispersion equation by finite element method (FEM) reflecting bio-chemical reaction, volatilization, and sorption/desorption as first order reaction model. Developed model was validated by comparing with analytic solutions and commercial software, CCHE2D.

In the second step, an algorithm for identifying significant reaction terms was proposed in order to operate the developed model efficiently. The algorithm is based on one-at-a-time sensitivity analysis for reaction parameters to find critical parameter values. Also, the applicability of the algorithm was examined by applying the developed model to Nakdong River, more specifically river reach between Gangjeong-Goryeong Weir and Dalsung Weir.

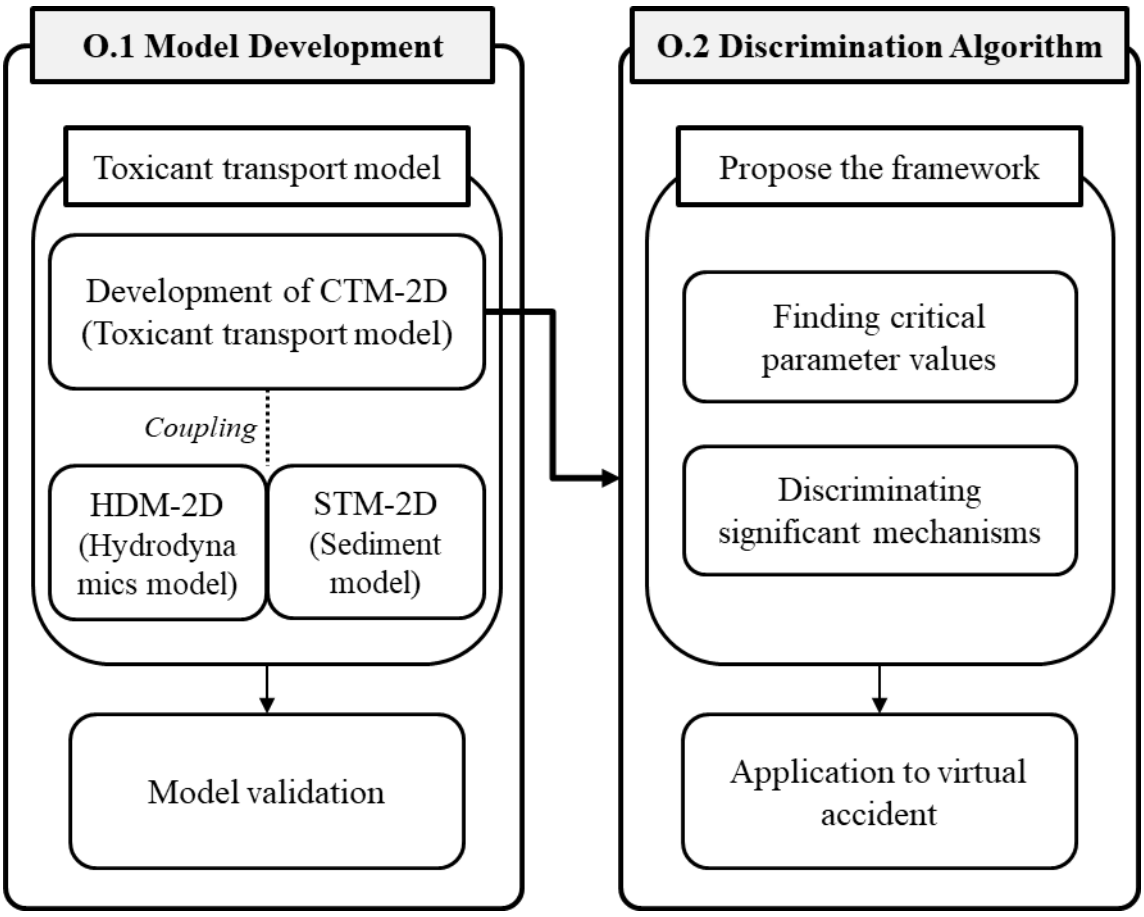


Figure 1.2 Thesis overview

2. Theoretical Research

2.1 Contaminant transport model in rivers

Rivers and reservoirs have been managed as major water resource, and many researchers have developed a variety of water quality models to manage the resource. Streeter and Phelps (1925) established the first water quality model (S-P model) to control river pollution in Ohio, USA, and various subsequent models have been developed over a long period of time. Since then, biochemical problems (plankton and heavy metals) have emerged, and high order models systems have been developed considering nitrogen and phosphorus analysis: QAUL model (Grenney et al., 1978; Brown and Barnwell, 1987), HSCTM2D (Hayter et al., 1999), RMA4 (Thomas and McAnall, 1985), WASP model (Ambrose et al., 1988; Ambrose et al., 1993; Artioli et al., 2005), EFDC (Tetra Tech, 2007) and CTM-2D (Lee and Seo, 2007). The features of these models are summarized in **Table 2.1**.

2.2.1 Two-dimensional contaminant transport model

The computation time of the contaminant transport model in the accident response system has a significant influence on the response time. Therefore, the computation time must be taken into consideration in selecting the model of the system. Rather than considering all of the complex mechanisms of nature, it will

Table 2.1 Representative contaminant transport models

Dimension	Model	Features
1D	Streeter-Phelps models	Streeter and Phelps established the first S-P model in 1925. S-P models focus on oxygen balance and one-order decay of BOD and they are one-dimensional steady-state models.
	QUAL (QUALI, QUALII, QUAL2E, QUAL2E UNCAS, QUAL-NIER, QUAL2K)	The USEPA developed QUAL I in 1970. QUAL models are suitable for dendritic river and non-point source pollution, including one-dimensional steady-state or dynamic models.
2D	HSCTM2D	The Hydrodynamic, Sediment, and Contaminant Transport Model Finite element modeling system for simulating two-dimensional, vertically-integrated, surface water flow (typically riverine or estuarine hydrodynamics), sediment transport, and contaminant transport.
	RMA4	Contaminant Transport Model The transport of a conservative contaminant or salinity intrusion in a system
	CTM-2D	Two-dimensional, vertically-integrated advection -dispersion model Based on finite element modeling system The transport of a non-conservative and conservative contaminant
3D	WASP (WASP1-7)	The USEPA developed WASP model in 1983. WASP models are suitable for water quality simulation in rivers, lakes, estuaries, coastal wetlands, and reservoirs, including one-, two-, or three-dimensional models.
	EFDC	Virginia Institute of Marine Science developed this model. The USEPA has listed the EFDC model as a tool for water quality management in 1997. EFDC model is suitable for water quality simulation in rivers, lakes, reservoirs, estuaries, and wetlands, including one-, two-, or three-dimensional models.

be more helpful to simplify the mechanism with significant factors of the phenomena. For example, it is possible to reduce the calculation time by simplifying the dimension of the analysis. Accordingly, one-dimensional model has been used for the accident response system such as QUAL2E and RiverSpill. However, it has limitation in representing the complex of river flow especially in the large rivers (Benedini and Tsakiris, 2013). In this cases, the higher dimensional models are used.

The pollutant in the river is transported through the three stages: near field, intermediate field, and far field as shown in **Figure 2.1**. When considering the scale of the fields, the analysis of the near field which requires 3-dimensional model is insignificant than the others since the pollutant is usually transported over the fields. On the other hand, the transport in the intermediate and far fields need to be analyzed. Especially, it is appropriate to use a two-dimensional model to analyze the domestic rivers because domestic rivers are made of intermediate fields where the transport is governed by transverse and longitudinal mixing.

There is a water quality analysis model called CTM-2D which is developed by Seoul National University (Lee and Seo, 2007). The depth-averaged form of the 2D advection-dispersion equation including the reaction term for non-conservative substances was used as the governing equation. Many studies have frequently used CTM-2D to simulate the pollutant transport in large rivers and small streams dealing with various water quality substances. Lee and Seo (2007), Lee and Seo (2010) applied this model to analyze the tidal current effect on the 2D behavior of BOD effluents accidentally in traduced from WWTPs in the Han River. Seo et al. (2016) and Park and Seo (2018) elucidated the 2D mixing characteristics of the conservative substance,

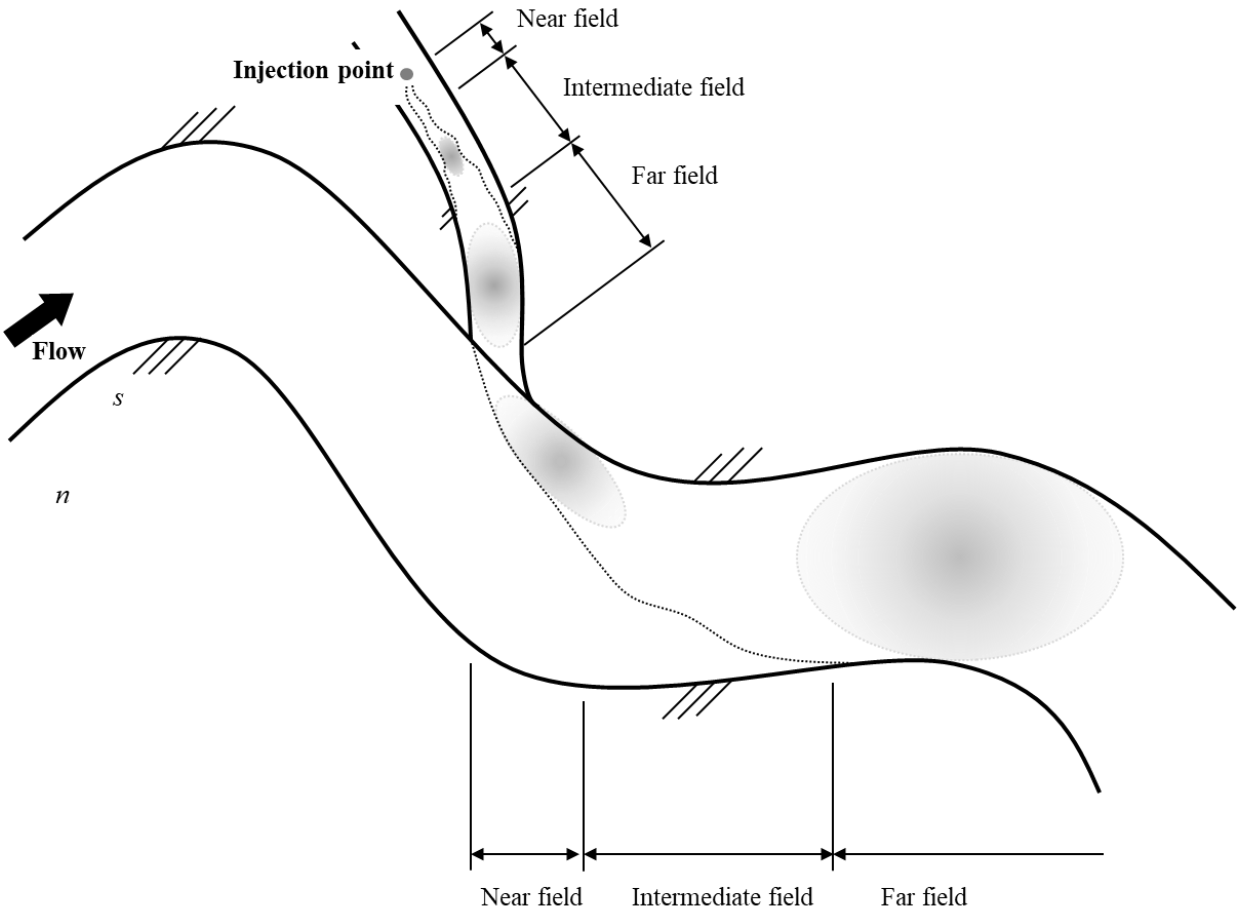


Figure. 2.1 Process of pollutant mixing in natural streams

Rhodamine WT in the meandering channels such as the Sum River and Hongcheon River, South Korea. Additionally, Kim et al. (2018) investigated the impact of thermal pollutants on the spatial distribution of of algae in the Nakdong River using CTM-2D.

2.2.2 Two-dimensional toxic chemical transport model

Table 2.2 shows detail comparison in terms of reaction terms of the toxic chemical transport models. All of models include the volatilization and extra reaction modules, as a first order decaying with rate of change coefficients such as

On the other hand, sorption process is pretty more complex, there are two kind of models: kinetic model, and equilibrium model. The kinetic model reflects sorption process as time dependent reaction, but the equilibrium model considers it to be immediately distributed when the pollutant is introduced in water. Many researches had figured out that the sorption process is time-dependent reaction. To represent general sorption process, this study also adopted kinetic model.

Table 2.2 Representative toxicant transport models and the features

Model	Dissolved Conc.	Sorption			Volatilization	Extra Reaction
		C_{db}	C_p	C_{pb}		
HSCTM2D (Hayter et al., 1999)	●	Kinetic model			-	$-\lambda C_d$
		-	●	●		
CCHE2D (Jia, 2013)	●	Equilibrium model			$-k_v C_d$	$-\lambda C_d$
		●	●	●		
CTM-2D (This study, 2019)	●	Kinetic model			$-k_v C_d$	$-\lambda C_d$
		-	●	●		
WASP (Ver. 8.1) (Wool et al., 2017)	●	Equilibrium model, Kinetic model			$-k_v C_d$	$-\lambda C_d$
		-	●	●		

2.2 Toxicant dynamics in river

When the toxicant is introduced into the water, the material experience the complex interacting physical, biogeochemical processes. **Figure 2.2** shows the general features of the transport of a toxic materials in the water. Introduced toxic contaminant in the water exists as dissolved and particulate form. These two forms of contaminant are basically dominated by the flow such as the advection and dispersion processes, but the additional reactions such as volatilization, sorption can be analyzed separately. The principal physical biogeochemical processes in the water column and sediment are (Thomann et al., 1987):

1. Adsorption and desorption between dissolved and particulate forms in the water column and sediment.
2. Settling and resuspension mechanisms of particulates between the sediment and the water column.
3. Diffusive exchange between the sediment and the water column.
4. Loss of the chemical due to biodegradation, volatilization, photolysis, and other chemical and biochemical reactions.
5. Gain of the chemical due to chemical and biochemical reactions.
6. Transport of the toxicant due to advective flow transport and dispersive mixing.
7. Net deposition and loss of chemical to deep sediments.

As above phenomena, the intricate mechanisms entangle each other, so previous researchers tried to simplify and constructed mathematical models of each mechanisms.

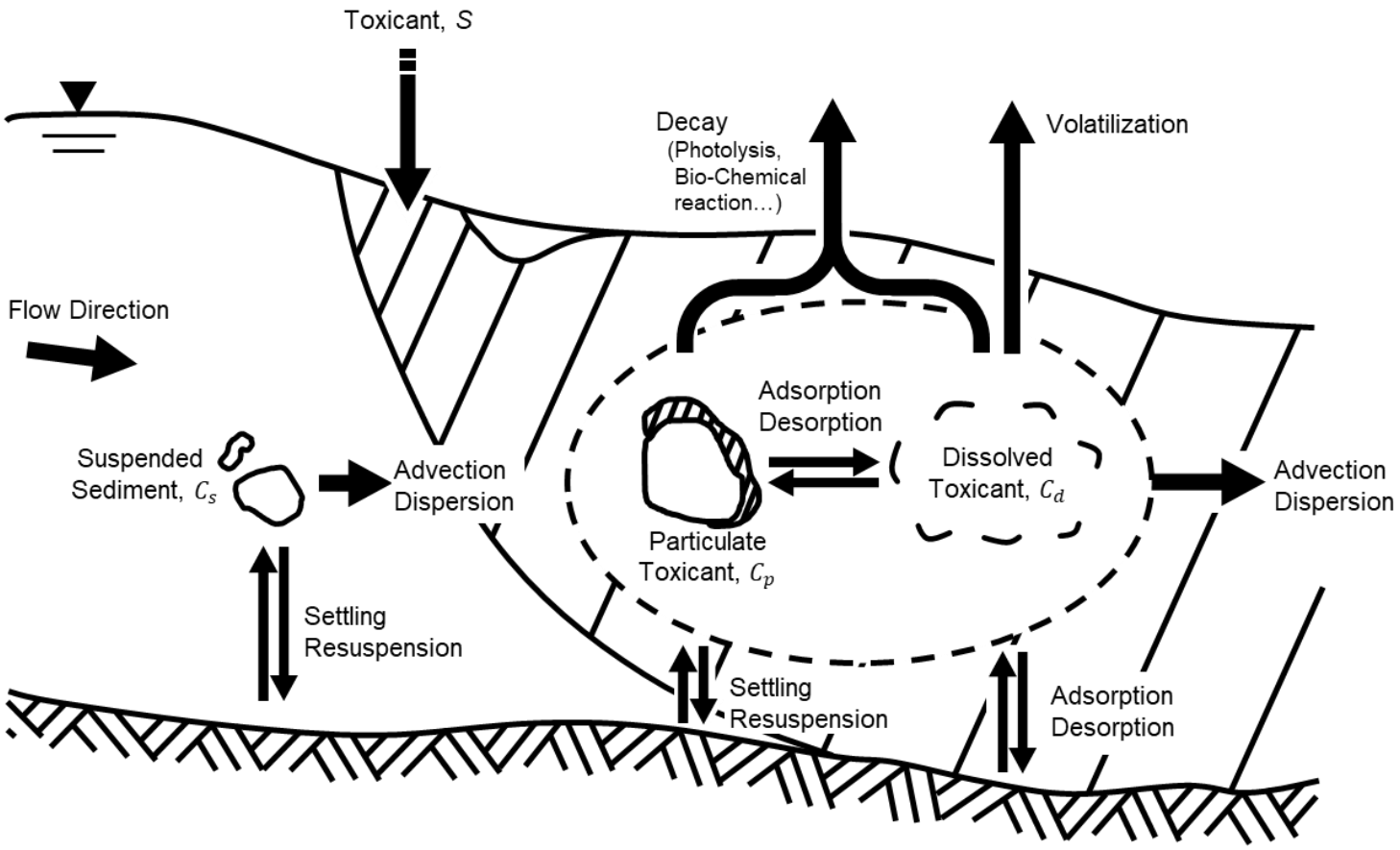


Figure 2.2 Schematic of principal features of physical-chemical reaction of toxic chemicals

2.2.1 Depth-averaged advection dispersion equation

In the large river, it is often be assumed that the mixing in the longitudinal and lateral direction dominate dispersion of pollutants due to the rapid completion of vertical mixing when injected to water (Yotsukura and Sayre, 1976; Rutherford, 1994; Jeon et al., 2007; Seo et al., 2016). Based on this fact, the 2D model which solves depth-averaged advection dispersion equation has been used in practical fields of river water quality modeling. The advection diffusion equation can be rewritten as below using the Reynold's decomposition and Taylor's analysis of turbulent shear flow.

$$\frac{\partial C}{\partial t}+\frac{\partial}{\partial x}(uC)+\frac{\partial}{\partial y}(vC)=\frac{\partial}{\partial x}\left[(e_x+D_L)\frac{\partial C}{\partial x}\right]+\frac{\partial}{\partial y}[(e_y+D_T)\frac{\partial C}{\partial y}] \quad \textbf{(2.1)}$$

where C is the depth-averaged concentration; u,v is averaged velocity along the x and y direction, respectively; D is the dispersion coefficient, and S is the sink/source term which can reflect the material's non-preserve characteristics. Since D_L and D_T are much larger than the e in rivers, Eq. 2.1 can be simplified as:

$$\frac{\partial C}{\partial t}+\frac{\partial (uC)}{\partial x}+\frac{\partial (vC)}{\partial y}=\frac{\partial}{\partial x}\left(D_L\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(D_T\frac{\partial C}{\partial y}\right)+S \quad \textbf{(2.2)}$$

The seven processes mentioned above summarize the exchange of pollutants occurring between the water body, suspended sediment, riverbed, and the bed pore. To

express this, the concentration of Eq 2.2 can be replaced by the dissolved concentration in the water body, the particulate concentration adsorbed to the suspended sediment, the dissolved concentration in bed pore water, and the particulate concentration adsorbed to bed materials. Accordingly, the reaction terms can be also substituted by the mass exchange between the phases such as adsorption / desorption.

2.2.2 Adsorption and desorption

2.2.2.1 Mathematical model

In the river, the mass transfer between water and soil takes place mainly by absorption, desorption, and dissolution. In addition, chemical reaction such as ion exchange between two phases and physical processes such as resuspension and sedimentation occur. Among them, the absorption and desorption of the components from the water body to the surface of the soil is the most important reaction (Tchobanoglous & Schroeder, 1985).

Adsorption is the process that the chemical sticks to the sediment, and desorption is the process of the adsorbed material move back into the water from the sediments. Earlier researchers reported that liquid-solid adsorption and desorption occurred rapidly, chemical equilibrium between the water and the material is achieved in a short time. Considering that their experiment progressed in only few hours and days, their results were assessed as unreasonable. Later studies in the late nineteenth century have carried out that the adsorption and desorption reactions are scales of the order of

several months and proved that underestimated results of the initial experimental researches (Karickhoff and Morris, 1985; Coates and Elzerman, 1986). The sorption process in rivers occurs with the macroscopic movement of pollutants and sediment. In other words, the sediment transports is relatively fast taking a few minutes and several hours, but the sorption takes several months. Therefore, it is necessary to analyze the change of concentration along a time in order to consider the absorption and desorption processes in the river.

The process can be understood as a diffusion process, and the partial differential equation can represent the temporal sorption process. There are two mathematical models for it: diffusion model and mass transfer model. The diffusion model modulates the diffusion between pore of the sediments and water body, and the equation can be written as

$$\frac{\partial \mathrm{C}_r}{\partial \mathrm{t}} = \frac{D}{r^2}\frac{\partial}{\partial \mathrm{r}}\left(r^2 \frac{\partial \mathrm{C}_\mathrm{r}}{\partial \mathrm{r}}\right) \quad \textbf{(2.3)}$$

where C_r is the concentration of contaminant in the porous particle as a function of r, r is the radial distance, and D is the diffusion coefficient. In the case of the mass exchange model, the mass is transferred by the difference between the average concentration in the pore and dissolved concentration with mass exchange rate. The model produces a simple approximate solution for computational efficiency. The equation is as follows.

$$\frac{\partial \overline{C_p}}{\partial t} = -k_s\left(\overline{C_p} - K_p C_w\right) \quad \textbf{(2.4)}$$

where C_p is the average concentration in the particles (kg / L); k_s is the mass exchange coefficient (1 / day); and K_p is the partition coefficient (L / kg).

In the case of river pollutant transport, it is generally modeled as a mass exchange model since advection and dispersion is dominant factors and it can reduce the calculation time. There are three layers (C_d- C_p- C_{pb}) and four layers (C_d- C_p- C_{db}- Cpb) models which are used for commercial software (Hayter et al., 1999; Jia et al., 2013; Riadh et al., 2014).

The mass transfer model described above shows the absorption / desorption between SS-water and bed-water as follows.

$$\frac{\partial C_p}{\partial t} = k_s\left(C_{p,eq} - C_p\right) \quad \textbf{(2.5)}$$

$$\frac{\partial C_{pb}}{\partial t} = k_s\left(C_{pb,eq} - C_{pb}\right) \quad \textbf{(2.6)}$$

where $C_{p.eq}$ and C_{pb} are in turn the equilibrium adsorption concentration between SS-water, bed-water; δ_m is the thickness of the mixed layer, which means the thickness of the layer where the contaminant can adsorb. Appendix. A explains detail models about mixing layer.

The use of mass transfer model to simulate such adsorption / desorption requires

parameters such as the soil-water partition coefficient and the sorption rate of the target stream. However, it is difficult to obtain parameter values on site when rapid simulations are needed, such as when dealing with toxic chemical spill accidents. Therefore, it is necessary to estimate the parameters from the constructed data. The studies of the estimation of each parameter by previous researchers are as follows.

2.2.2.2 Partitioning coefficient and rate of sorption

The soil - water partition coefficient is the ratio of the amount of dissolved material in the waterbody and the amount of form of particles on the sediment. It is used to define the approximate distribution of contaminants between two systems. To simulate adsorption, the soil-water partition coefficient is defined as:

$$\mathrm{K_P} = \frac{\text{Particulate Conc.}}{\text{Dissolved Conc.}} = \frac{m_p/m_s}{m_d/V_w} = \frac{m_p/m_s}{m_d/V_{w+s}} \quad \textbf{(2.7)}$$

where V_w, V_{w+s} is the volume of the water, and volume of the water and sediment; M_p, M_s, M_d is the mass of the particulate pollutant, suspended sediment, and dissolved pollutant, respectively. In addition, if the amount of suspended sediment in a unit volume is small, the total volume of the water and sediment is almost equal to the volume of the water, so V_{w+s} can be rewritten as V_w. The equilibrium concentration can be obtained by multiplying two types of concentration and K_p as follow:

$$C_{p,eq} = K_p C_d C_s \quad \textbf{(2.8)}$$

where $C_{p,eq}$ is equilibrium concentration of particulate form. Thus, the difference between the obtained equilibrium concentration and current particulate contaminant concentration is obtained, and the exchange rate between two forms can be approximated by this approach.

When an arbitrary substance is introduced into a river, the soil-water partition coefficient of the substance is not known. Previous researchers have studied to estimate the soil-water partition coefficient by expanding the octanol-water partition coefficient. (Karickhoff, 1979; Karickhoff, 1984). The coefficient is used in various fields such as the analysis of drug absorption, penetration etc. in the pharmaceutical industry. The octanol - water partition coefficient of the most of substances are known. Previous researchers have found that this octanol-water partition coefficient has a linear relationship with the organic carbon-water partition coefficient in the log scale (Karickhoff, 1984), the relationship is expressed by following equation.

$$K_d = f_{oc} K_{oc} \quad \textbf{(2.9)}$$

$$K_{oc} = \beta \times (K_{ow})^{\alpha} \quad \textbf{(2.10)}$$

where f_{oc} is fraction of the organic carbon of the sediment, K_{oc} is the soil organic carbon-water partitioning coefficient, and the α, β is regression coefficients which

were determined by previous researchers and tabulated in **Table. 2.3**.

In the 2000s, the distribution coefficient of each substance used in specific fields such as new medicines and pesticides was studied, and the soil-water partition coefficient was estimated through the water-octanol partition coefficient of neutrons and ions of the substances (Scheytt et al., 2005; Franco and Trapp, 2008; Yamamoto et al., 2009; Kozerski et al., 2014). In this study, the estimation equation proposed by Karickhoff (1981) was adopted because the water quality model for the hazardous chemical would be applied only to the hydrophobic materials for reflecting the sorption mechanism.

As aforementioned, it is necessary to analyze the time-dependent change of the concentration by sorption process (Kan et al., 1994; Lick, 2009). Karickhoff and Morris (1985) suggested the relationship between the absorption and desorption rates of hydrophobic materials and the soil-water partition coefficient as follows.

$$k_s = (0.03K_d)^{-1} \quad \textbf{(2.11)}$$

where k_s is The rate of change per hour by the sorption rate between soil and water [1/h]; unit of K_d is l/kg; and the correlation coefficient (r) is 0.87. Also, Brusseau and Rao (1989) suggested another relationship which of the correlation coefficient (r) is 0.97.

$$\log k_s = 0.301 - 0.668 \log K_p \quad \textbf{(2.12)}$$

Two formula above were evaluated not to represent the slow-scale sorption mechanism (Kan et al., 1989). However, when considering the flow velocity in the case of chemical spill accidents, only the fast sorption mechanism may be considered so that the developed model can selectively use Eq 2.15 and Eq 2.16.

Table 2.3 Regression coefficient between soil-water and organic carbon-water partitioning coefficient

Auther	# of Materials	log K_{ow}	$\beta x10^3$	α	r
Kenaga and Goring, 1980	45	-1.7~6.6	24.00	0.54	0.93
Rao and Davidson, 1980	15	-0.5~5.6	0.66	1.03	0.95
Karickhoff, 1981	6	1.0~6.5	0.45	0.99	0.99
Schwarzenbach and Westall, 1981	12	2.6~4.7	3.10	0.72	0.97
Chiou et al., 1983	12	2.1~5.6	0.30	0.9	0.99
Mingelgrin and Gerstl, 1983	7	3.1~6.2	1.10	0.87	0.85
Karickhoff, 1983	10	2.1~6.6	0.63	1	1
Mingelgrin and Gerstl, 1983	7	3.1~6.2	1.10	0.87	0.85
Curtis et al., 1986	22	1.4~6.6	0.59	0.92	0.94
Pussemier et al., 1990	11	2.11-5.18	0.29	1.01	0.96
Gao et al., 1996	119	`-3.00~9.7	5.94	0.7495	0.9139
Girvin and Scott, 1997	3	4.7~7.1	0.11	1.07	0.98

**K_{ow} [-], K_{oc}[m3/kg]

2.2.3 Deposition and resuspension

Mass transfer between water and soil occurs due to the sedimentation and resuspension of the suspended sediments. In this case, the concentration is transported as two forms of the adsorbed and dissolved contaminants. That is, when suspended, not only the substance adsorbed on the bed but also the concentration of the bottom pore water are exchanged together. When sedimentation occur, the concentration of the dissolved substance in the water body as well as the substance adsorbed on the suspended sediment. Wu (2008) proposed a mathematical model for the exchange of chemicals due to sedimentation / resuspension in a two-dimensional model based on the conservation of mass.

$$\frac{\partial C_p}{\partial \mathrm{t}} = \frac{1}{h}\left[\max(E_b - D_b, 0)\frac{\left(C_p\right)_B}{1-\phi} + \min(E_b - D_b, 0)\frac{C_p}{s}\right] \quad \textbf{(2.13)}$$

$$\frac{\partial C_d}{\partial \mathrm{t}} = \frac{1}{h}\left[\max(E_b - D_b, 0)\frac{\phi}{(1-\phi)}\frac{(C_d)_B}{\phi} + \min(E_b - D_b, 0)\frac{\phi}{(1-\phi)}\frac{C_d}{1-s}\right] \quad \textbf{(2.14)}$$

where E_b and D_b are the suspended and sedimentation velocities, respectively, and are the values calculated from the model; φ is the bed porosity; and s is the ratio of volumes of water and SS.

As a result, the contaminant transport by sedimentation and resuspension of the sediment is determined by the characteristics of suspended sediment. In analyzing the transport of SS in streams, the size of the particles is a fundamental property, which is sufficient to explain the physical properties of the particles. According to this, sediment is classified into 6 types as clay, silt, sand, gravel, zebra, and oval according to the size of particle size, and the standard of sediment type proposed by Lane (1947) shown in Table 2.5 are generally used. It is also possible to distinguish the cohesiveness of sediment by 0.062 mm (particle size that distinguishes sand and silt, Table 2.5), assuming that most of sediment transfers occurs as suspended sediment.

The transportability of non-cohesive sediment (sand, gravel) is determined by the potential transport capability of the flow. In other words, sedimentation occurs when the difference between the concentration of SS in the waterbody and potential transfer ability is positive, and erosion occurs when it is negative. This vertical direction transport can be expressed by the following mathematical expression.

$$\frac{\partial C_s}{\partial t} = \frac{W_s}{h}(C_{s,eq} - C_s) \quad \textbf{(2.14)}$$

where C_s is the concentration of suspended sediment, W_s is the settling velocity (m / s) and $C_{s,\,eq}$ is the the equilibrium concentration of the non-cohesive sediment.

Since there are dozens of related equilibrium formulas and there is a large difference in the results according to the formulas, the proper formula need to be selected suitable for

the simulation area.

Cohesive sediment (silt, clay, etc.) is a mixture of inorganic minerals, organic and biochemicals are usually composed of it. Therefore, the erosion sedimentation characteristics are strongly influenced by the coagulation phenomena between particles, and the cohesive strength also varies depending on the composition of the material, the particle size distribution, and the organic matter content (Mehta, 1986). Therefore, it is common to analyze the mechanisms of erosion and sedimentation separately as follows.

$$\frac{\partial \mathrm{C_s}}{\partial t} = Q_e - Q_d \qquad \textbf{(2.15)}$$

where Q_e and Q_d represent the changes in the concentration of suspended sediment by erosion and sedimentation, respectively.

2.2.4 Volatilization and biochemical reaction

The biochemical reaction and volatilization processes are usually assumed as a linear process as

$$\frac{\partial C}{\partial t} = \lambda(C_{eq} - C) \qquad \textbf{(2.16)}$$

where λ is degradation rate coefficient which includes biochemical reaction and

volatilization. These processes are usually considered as one inclusive action. In other words, the terms of bio-chemical reaction and volatilization in Eq. 2.3 are regarded as a term. However, the volatilization of some toxic chemical contributes significantly to the determination of the ultimate fate of any of organics that might be discharged into our streams and rivers (Rathbun and Tai, 1981), so the two processes need to be interpreted separately.

The bio-chemical reaction coefficient of significant toxic substances have been investigated. On the other hand, it is difficult to define volatilization coefficient because the value differs depending on not only the materials but also flow characteristics such as water depth and velocity. Accordingly, this value of a material can be estimated from the reaeration which is the volatilization process of oxygen. The reaeration rate coefficient can be estimated as (Tchobanoglous and Schroeder, 1985)

$$k_r = 294\left(D_{\mathrm{aq},O_2} u\right)^{\frac{1}{2}} / \overline{H}^{\frac{3}{2}} \qquad \textbf{(2.17)}$$

where k_r is reaeration rate coefficient [1/d], D_{L,O_2} is diffusion coefficient of oxygen [m^2/d] which is 1.760×10^{-4} m^2/d at 20℃, u is stream velocity [m/s], and $\overline{\mathrm{H}}$ is stream depth [m].

Many researchers have shown through laboratory experiments that the volatility and volatilization coefficients of any volatile chemicals are constant. This means that if the re-aeration coefficient in nature can be measured, the volatility coefficient of any volatile chemical can be estimated. The ratio between volatilization coefficient of the

arbitrary material and reaeration coefficient in the laboratory can be expressed as a function of the ratio of diffusion coefficients of the material and oxygen in water. For highly volatile chemicals (substances with strong liquid film resistance), the ratio can be estimated as follows (Dobbins, 1964; Lee, 1973).

$$(k_v^C/k_v^O)_{lab} = f\left(D_{aq}^C/D_{aq}^O\right) = \left(D_{aq}^C/D_{aq}^O\right)^{\mathrm{n}} \quad \textbf{(2.18)}$$

where the value of n varies between 0.5 and 1 depending on the mixing condition, and in natural streams it has a value between 0.5 and 0.65 (Skelland, 1974; Smith et al., 1980; Roberts and Dandliker, 1983; Ince and Inel, 1989). Therefore, the volatility coefficient estimation in this study is shown in Eq. 23, and the value of n is 0.6 (Smith et al., 1980).

$$k_v = k_r \left(\frac{D_{aq}}{D_{aq}^{O_2}}\right)^n \quad \textbf{(2.19)}$$

3 Model development

3.1 Description

This study adopted the depth-averaged 2D numerical models to simulate the spatiotemporal distribution of toxic chemical concentration and flow fields. To generate the flow velocity and water depth, a hydrodynamic simulation was performed by HDM-2D which is shallow water flow model. For water quality simulation, 2D contaminant transport model, CTM-2DT, was developed to analyze the toxic chemicals transport. To obtain the suspended sediment distribution to simulate the sorption process of the toxic chemical, sediment transport model, STM-2D was developed. As shown in Figure 3.1, CTM-2DT was coupled with HDM-2D which provides the input variable of CTM-2DT such as velocity fields and water depth. CTM-2DT was also coupled with STM-2D which provides sediment concentration fields. To implement the complex geometry of natural streams including confluence and meandering zones, the coupled system of HDM-2D, CTM-2DT, and STM-2D was solved using the finite element method (FEM) with the combination of structured and unstructured grids. The numerical models were constructed adopting the weighted residual method based on the Streamline-Upwind Petrov-Galerkin (SUPG) formulation (Brooks and Hughes, 1982).

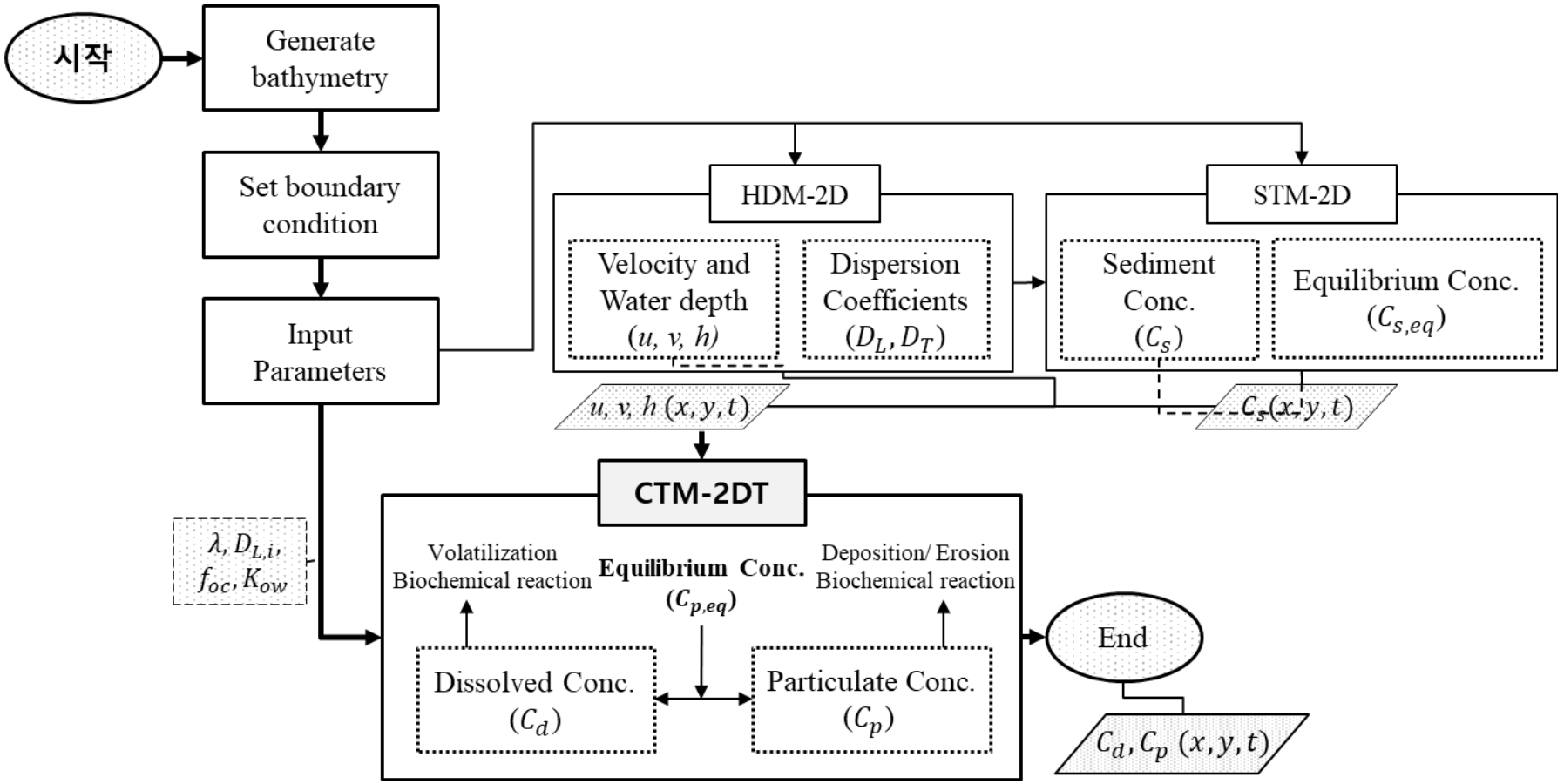


Figure 3.1 Flowchart of numerical modeling for fate of toxic chemical

3.1.1 Governing equations

Toxic chemicals are transported together with complex mechanisms such as sedimentation, resuspension, volatilization, and the sorption process as shown in Figure 2.2. In this study, C in Equ 2.2 was changed to Cd, Cp and Cpb to add a reaction term representing the sorption, sedimentation, resuspension, volatilization and biochemical reaction of each phase. Each reaction can be represented by a first reaction process and expressed as follows.

$$S_d = -k\left(K_p C_d C_s - C_p\right) - k\left(\frac{\delta_m}{h} K_p C_d (C_s)_B - C_{pb}\right) - v_v C_d - \lambda C_d \quad \textbf{(3.1)}$$

$$S_p = +k\left(K_p C_d C_s - C_p\right) - \alpha \frac{W_s}{h}\left(C_p - C_{p,eq}\right) - \lambda C_p \quad \textbf{(3.2)}$$

$$\left(S_p\right)_B = +k\left(\frac{\delta_m}{h} K_p C_d \rho_b - C_{pb}\right) + \alpha \frac{W_s}{h}\left(C_p - C_{p,eq}\right) \quad \textbf{(3.3)}$$

where S_d, S_p, and $S_p b$ are the sink/source terms of the dissolved concentration, the particulate concentration on the SS and riverbed, respectively; δ_m is the thickness of the mixing layer, and $C_{p,\,eq}$ is the equilibrium adsorptive concentration due to suspension and sedimentation.

In order to simulate each term, input parameters are required. In the developed model, the estimation equation is adopted as shown in Table 3.1. First, partition coefficient regression equation proposed by Karickhoff (1981) were used to estimate the water - soil partition coefficient (K_p).

$$K_{oc} = 0.63 \times 10^{-3} \times K_{ow} \quad \textbf{(3.4)}$$

$$K_d = f_{oc} K_{oc} \quad \textbf{(3.5)}$$

where the water-octanol partition coefficient (K_{ow})is dimensionless, and m^3/kg for the water-organic carbon partition coefficient (K_{oc}). Because hydrophilic materials can act as exchange factors between water and soil, such as biochemical reactions, Karickhoff's (1981) study of hydrophobic materials has been used. In addition, the sorption exchange rate (k) can be selectively used in Equation 2.15 and Equation 2.16. The thickness of the mixed layer is 0.1 ~ 0.2 times the depth of the water as suggested by Karim and Kennedy (1982). The parameter for estimating the volatility term is the volatility coefficient. The volatile coefficient can be expressed as a function related to the water diffusion coefficient (D) and water temperature of the target material (Dobbins, 1964; Lee, 1973). As for the diffusion coefficient, the values for most materials are known as well as the water - octanol partition coefficient, and the reaeration coefficient varies with the water temperature.

3.1.2 Hydrodynamic model (HDM-2D), sediment transport model (STM-2D)

As mentioned above, we used HDM-2D, a flow analysis model, to predict flow velocity and depth. The governing equations of this model are the two-dimensional shallow water equations with the momentum and mass conservation equations as the water depth averages, assuming barotropic and hydrostatic assumptions, as shown below.

$$\frac{\partial \mathrm{u}_i}{\partial t} + \mathrm{u_j}\frac{\partial \mathrm{u}_i}{\partial x_j} = -g\frac{\partial (z+h)}{\partial x_i} + \frac{1}{h}\frac{\partial}{\partial x}\left(h\nu_t \frac{\partial u_i}{\partial x_j}\right) - gn^2\frac{u_i\sqrt{u_j u_j}}{h^{4/3}} \qquad \textbf{(3.6)}$$

$$\frac{\partial h}{\partial t} + h\frac{\partial u_j}{\partial x_j} + u_j\frac{\partial h}{\partial x_j} = 0 \qquad \textbf{(3.7)}$$

where t is the time; $\mathrm{u_i}$ and $\mathrm{u_j}$ are the depth-averaged velocity components; g is the acceleration of gravity; z is the bed elevation; h is the flow depth; ν_t is the kinematic eddy viscosity; and n is the Manning's roughness coefficient. To determine ν_t, Smagorinsky turbulent model was used in HDM-2D as:

$$\nu_t = \left(C_s\Delta_g\right)^2\sqrt{2\bar{S}_{ij}\bar{S}_{ij}} = \left(C_s\Delta_g\right)^2|\bar{S}| \qquad \textbf{(3.8)}$$

where C_s is the Smagorinsky coefficient; Δ_g is the grid size; $\bar{S}_{ij}$ is the tensor of strain rate; and $|\bar{S}| = \sqrt{2\bar{S}_{ij}\bar{S}_{ij}}$. C_s is predetermined as a constant number, typically 0.3 or less, depending on the flow configuration (Law, 2010).

HDM-2D has been used in many studies to solve the shallow water problems in open channels. Song and Seo (2010) elucidated the influence of wall boundary conditions and imposition of lateral velocity boundary conditions on the flow filed using this model. Moreover, Song et al. (2012) analyzed the secondary current effect on the lateral velocity profile to enhance the model. Song et al. (2017) also adopted floodplain. Park and Song (2018) used HDM-2D to simulate the dispersion of the pollutants considering the change of the flow directions induced by the tidal current at the river mouth of the Han River, South Korea.

In order to simulate sediment resuspension and sedimentation of suspended sediment, STM-2D, a depth-averaged sediment transport model, was used. The finite element method using the SUPG technique is used to analyze the depth-averaged advection dispersion equation and its governing equations are as follows (Jeon, 2010).

$$\frac{\partial C_s}{\partial t} + u\frac{\partial C_s}{\partial x} + v\frac{\partial C_s}{\partial y} - \nabla \cdot \left(D_{ij}\nabla C_s\right) = \frac{W_s}{h}\left(C_{s,eq} - C_s\right) \qquad \textbf{(3.9)}$$

where D_{ij} is the dispersion tensor which can be decomposed longitudinal and transverse direction as explained in previous chapter; and *S*(C, t) is the term to reflect the resuspension and settling of the suspended sediment.

The sedimentation and resuspension depend on the cohesiveness of the sediment. In the case of non-cohesive sediment, the ability is determined by the potential transport capacity of the flow. In other words, sedimentation takes place when the concentration of suspended solids is less than the equilibrium concentration, and resuspension occurs when it is larger. Although 12 estimation equations have been proposed, the results of each equation show significantly different values. Therefore, the equation should be chosen carefully considering flow and stream conditions. The STM-2D allows the user to select an appropriate model, and the loaded equations are shown in **Table 3.1** along with the characteristics.

Table 3.1 Representative suspended sediment transport models and the features

Author	Equation	Features
Engelund and Hansen (1972)	$C_{eq} = 0.05\frac{\gamma_s}{\gamma}\frac{U}{h}\left(\frac{D}{g\left(\frac{\gamma_s}{\gamma}-1\right)}\right)^{\frac{1}{2}}\left(\frac{\tau_b}{(\gamma_s-\gamma)D}\right) \times 10^6$	- dune - D >0.15 mm (upper flow regime)
Shen and Hung (1972)	$\log C_{eq} = -107404.45938164 + 324214.74734085Y$ $-326309.58908739Y^2 + 109503.87232539Y^3$	- Experimental channel, small rivers
Yang (1973)	$\log C_{eq} = 5.435 - 0.286\log\frac{\omega_s D}{\nu} - 0.457\log\frac{U^*}{\omega_s}$ $+\left(1.799 - 0.409\log\frac{\omega_s D}{\nu} - 0.314\log\frac{U^*}{\omega_s}\right)\log\left(\frac{US}{\omega_s} - \frac{U_{cr}S}{\omega_s}\right)$	- Regression by the variable of Unit stream power) for sand
Yang (1979)	$\log C_{eq} = 5.165 - 0.153\log\frac{\omega_s D}{\nu} - 0.297\log\frac{U^*}{\omega_s}$ $+\left(1.780 - 0.360\log\frac{\omega_s D}{\nu} - 0.480\log\frac{U^*}{\omega_s}\right)\log\left(\frac{US}{\omega_s}\right)$	- Regression by the variable of Unit stream power) for sand - C > 100 ppm
Ackers and White (1973)	$C_{eq} = \frac{G_{gr}D}{h}\frac{\gamma_s}{\gamma}\left(\frac{U}{U^*}\right)^n$	- D > 0.04 mm - Froude number < 0.8

3.2 Model validation

3.2.1 Soil – water reaction

To verify the soil - water related mechanism of the developed model, simulation is conducted under several conditions with assumptions to compare the analytic and the numerical solution. To simplify the problem, the two-dimensional transport diffusion equation in stagnant water assuming zero velocity and no time-space variations in depth can be written as:

$$\frac{\partial \mathrm{C_d}}{\partial \mathrm{t}} = -k\left(K_p C_d C_s - C_p\right) - k\left(\frac{\delta_m}{h} K_p C_d (C_s)_B - C_{pb}\right) \quad \textbf{(3.10)}$$

$$\frac{\partial \mathrm{C}_p}{\partial \mathrm{t}} = +k\left(K_p C_d C_s - C_p\right) \quad \textbf{(3.11)}$$

$$\frac{\partial \left(\mathrm{C}_p\right)_B}{\partial \mathrm{t}} = +k\left(\frac{\delta_m}{h} K_p C_d (C_s)_B - C_{pb}\right) \quad \textbf{(3.12)}$$

When concentration is injected into a static space, the diffusion term is also treated as zero since the concentration gradient in the transverse direction is very small. In this simplified condition, the verification was performed by establishing the condition that only a single mechanism occurs among the three mechanisms between soil and water.

3.2.1.1 Validation with analytic solution (C_d - C_p)

In order to verify the mass exchange model between the dissolved concentration and the adsorbed concentration on the suspended sediment, the verification was carried out under the conditions of the uniform and the steady flow which do not flow in the square channel.

$$\frac{\partial C_d}{\partial t} = -k\left(K_p C_d C_p - C_p\right) \quad \textbf{(3.13)}$$

$$\frac{\partial C_p}{\partial t} = k\left(K_p C_d C_p - C_p\right) \quad \textbf{(3.14)}$$

When taking the above equation as the Laplace transform for t, the solution can be rewritten as follow

$$C_p = -\left(AC_{d0}\frac{e^{t(A-B)}}{A-B} + \frac{A}{B-A}\right) \quad \textbf{(3.15)}$$

$$C_d = \quad AC_{d0}\frac{e^{t(A-B)}}{A-B} + \frac{B}{B-A} \quad \textbf{(3.16)}$$

$$A = -k_s K_p (C_s)_B$$

$$B = k_s \quad \textbf{(3.17)}$$

The concentrations of suspended sediments and water-octanol partition coefficients were set to various values as shown in **Table 3.2a**. The initial concentration

of dissolved concentration was injected with 1 kg/m^3, and the organic carbon ratio of the bed material, f_{oc}, was 0.01, and the porosity was maintained at 0.4. The water - octanol partition coefficient was used in the range, ($\log(K_{ow}) = 2\sim2.7$), of one of hydrophobic substances out of 38 substances. In addition, the time interval (Δt) was 0.001 hour (3.6 seconds). **Figure 3.2** shows the result, with a maximum error less than 0.1%.

Table 3.2 Validation cases for each reactions

C_0 (kg/m^3)	U (m/s)	H (m)	Δt (sec)	K_{ow}	C_s (ppm)	$CASE\#$
1	0	1	36	100	500	SS11
					1000	SS12
					1500	SS13
				250	500	SS21
					1000	SS22
					1500	SS23
				500	500	SS31
					1000	SS32
					1500	SS33

(a) Validation cases for sorption to suspended sediment

C_0 (kg/m^3)	U (m/s)	H (m)	Δt (sec)	K_{ow}	δ_m (m)	$CASE\#$
1	0	1	36	100	0.1	BS11
					0.15	BS12
					0.2	BS13
				250	0.1	BS21
					0.15	BS22
					0.2	BS23
				500	0.1	BS31
					0.15	BS32
					0.2	BS33

(b) Validation cases for sorption to riverbed

C_0 (kg/m^3)	Δt (sec)	Δx (m)	U (m/s)	H (m)	D_{aq} (m^2/day)	k_v (/day)	$CASE\#$
1	2	2	0.25	2	0.00005	0.3240	VT111
					0.00010	0.4912	VT112
				5	0.00005	0.0820	VT121
					0.00010	0.1243	VT122
			0.5	2	0.00005	0.4583	VT211
					0.00010	0.6946	VT212
				5	0.00005	0.1159	VT221
					0.00010	0.1757	VT222

(c) Validation cases for volatilization

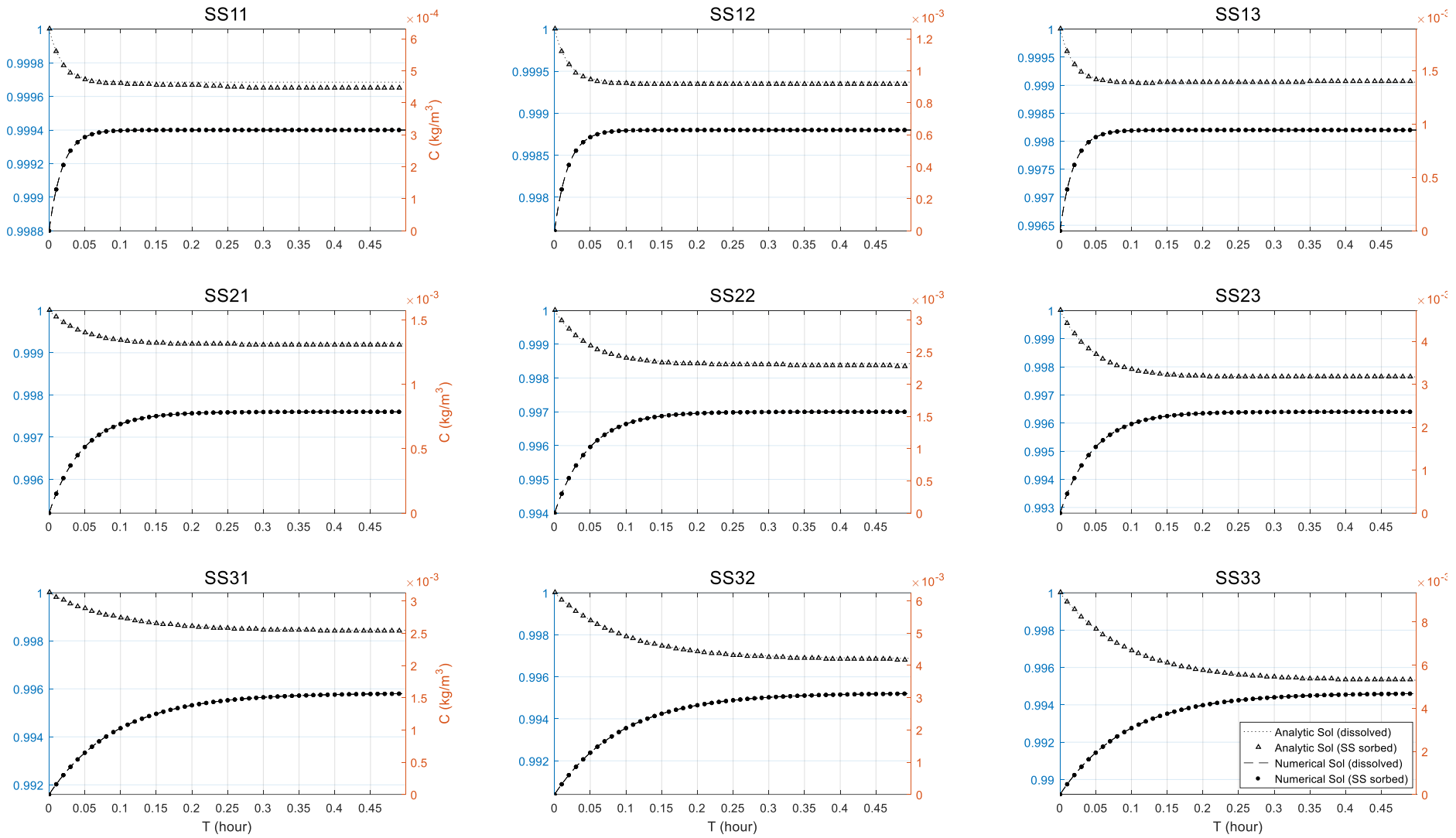


Figure 3.2 Validation results of sorption to suspended sediment

3.2.1.2 Validation with analytic solution (C_d - C_{pb})

In order to verify the mass exchange model between the dissolved concentration and the adsorbed concentration in the bed, the same conditions were used as in the 3.2.1.1.The verification was carried out under the conditions of the uniform and the steady flow which do not flow in the square channel with sorption process with bed only.

$$\frac{\partial C_d}{\partial t} = -k\left(\frac{\delta_m}{H} K_p C_d (C_s)_B - \left(C_p\right)_B\right) \quad \textbf{(3.18)}$$

$$\frac{\partial \left(C_p\right)_B}{\partial t} = k\left(\frac{\delta_m}{H} K_p C_d (C_s)_B - \left(C_p\right)_B\right) \quad \textbf{(3.19)}$$

When taking the above equation as the Laplace transform for t, the solution can be rewritten as follow

$$C_p = -\left(AC_{d0}\frac{e^{t(A-B)}}{A-B} + \frac{A}{B-A}\right) \quad \textbf{(3.20)}$$

$$C_d = \quad AC_{d0}\frac{e^{t(A-B)}}{A-B} + \frac{B}{B-A} \quad \textbf{(3.21)}$$

$$A = -\frac{\delta_m}{H} k_s K_p (C_s)_B$$
$$B = k_s \quad \textbf{(3.22)}$$

The water-octanol partition coefficient was set to various values as shown in **Table 3.2b**. The initial concentration of dissolved concentration was injected with 1 kg/m^3, and the organic carbon ratio of the bed material, f_{oc}, was 0.01, and the porosity was maintained at 0.4. The water - octanol partition coefficient was used in the range, ($\log(K_{ow}) = 2 \sim 2.7$), of one of hydrophobic substances out of 38 substances. In addition, the time interval (Δt) was 0.001 hour (3.6 seconds). **Fig 3.2** shows the result, with a maximum error less than 0.1%.

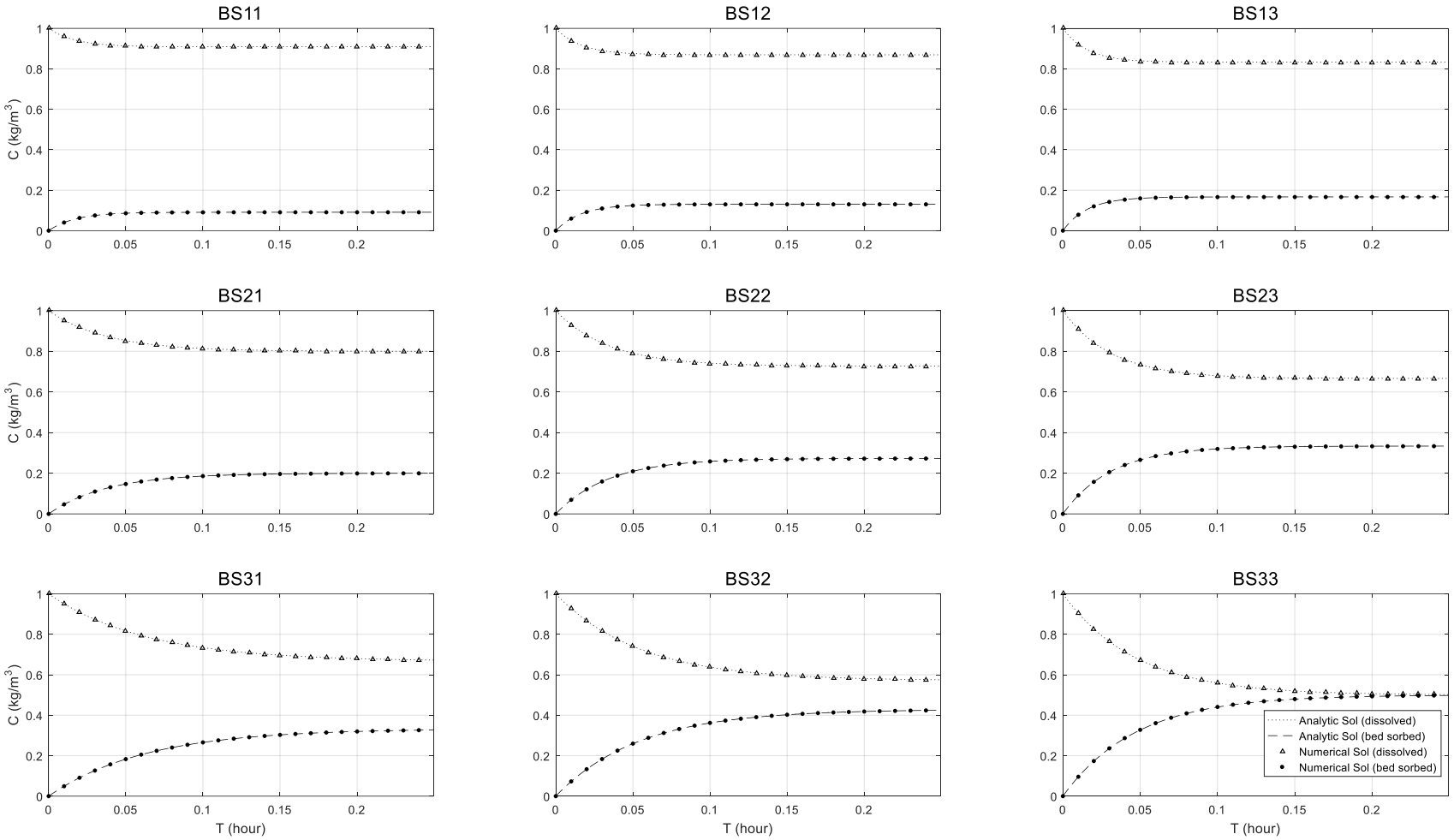


Figure 3.3 Validation results of sorption to riverbed

3.2.2 Validation of volatile term

3.2.2.1 Continuous injection in rectangle channel

In order to verify the developed volatilization model, continuous line injection simulations were performed in a virtual rectangular water channel with constant water depth and flow rate. To simplify the problem, assuming that there is no spatio-temporal variation of the dispersion coefficient, the two-dimensional transfer diffusion equation can be written as

$$\frac{\partial \mathrm{C}}{\partial \mathrm{t}} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} - D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) = -k\left(C - C_{eq}\right) \tag{3.23}$$

where C = concentration; u, v = flow velocity in the x and y directions [m/s]; D = diffusion coefficient [m^2/s]; k = attenuation coefficient [1/day]. The flow conditions and boundary conditions for simulating a constant concentration injection from the left are as follows.

$$\begin{gathered} \mathrm{C} = \mathrm{C}_0 \ \text{at} \ \mathrm{x} = 0, \qquad \forall \mathrm{t} \\ \mathrm{C} = 0 \quad \text{at} \ \mathrm{x} > 0, \qquad \mathrm{t} = 0 \\ \frac{\partial \mathrm{C}}{\partial x} = 0 \ \text{at} \ \mathrm{x} = \mathrm{L} \\ \frac{\partial \mathrm{C}}{\partial y} = 0 \ \text{at} \ \mathrm{y} = \pm \mathrm{W}/2 \\ U = U \ \text{for the plane} \\ \mathrm{V} = 0 \ \text{for the plane} \end{gathered} \tag{3.24}$$

where C_0 is the injection concentration [kg/m^3], L is the length of the channel, and W is the channel width. When the defined flow condition and boundary condition are substituted into Eq 3.23, the governing equations and boundary condition equations are summarized as follows. Especially, when the transverse velocity is zero, the transverse diffusion term can be treated as zero since the concentration gradient in the transverse direction is very small.

$$\frac{\partial \mathrm{C}}{\partial t} + U\frac{\partial \mathrm{C}}{\partial x} - D_x\frac{\partial^2 \mathrm{C}}{\partial x^2} = kC \qquad \textbf{(3.25)}$$

As a result, it is simplified to a one-dimensional problem, and the analytic solution can be obtained as

$$C = \frac{C_0}{2}\left[erfc\left(\frac{x-ut}{\sqrt{4Dt}}\right) + erfc\left(\frac{x+ut}{\sqrt{4Dt}}\right)\exp\left(\frac{ux}{D}\right)\right]\exp\left(-\frac{\mathrm{k}}{3600*24}\frac{\mathrm{x}}{\mathrm{u}}\right) \qquad \textbf{(3.26)}$$

By comparing these with numerical solutions, the model can be confirmed while the governing equations are well established or not. The error of the numerical solution is calculated by the ratio of the analytic solution to the difference between numeric and analytic solutions as

$$Error = \frac{|C_{exact} - C_{numeric}|}{C_{exact}} \times 100\ (\%) \qquad \textbf{(3.27)}$$

3.2.2.2 Validation with analytic soluation

The equation for estimating the volatility coefficient is rewritten as Eq 3.28 (Smith et al., 1980).

$$k_v = 294\left(D_{\mathrm{L},O_2}u\right)^{\frac{1}{2}}/\overline{H}^{\frac{3}{2}}\left(\frac{D_L}{D_L^{O_2}}\right)^{0.6} \tag{3.28}$$

Considering the uniform and steady conditions, the volatility coefficient for the entire simulated section will have a single value, so the given condition can be obtained as the volatility coefficient through Eq 3.28. Therefore, it is possible to compare the numerical solution by the volatilization module of the developed model and the analytical solution obtained by substituting the volatilization coefficient into Eq. 3.28. **Table 3.2c** summarizes the verification conditions. As a result of the simulation, the error is less than 0.1% as shown in Fig. 3, and the program is well established.

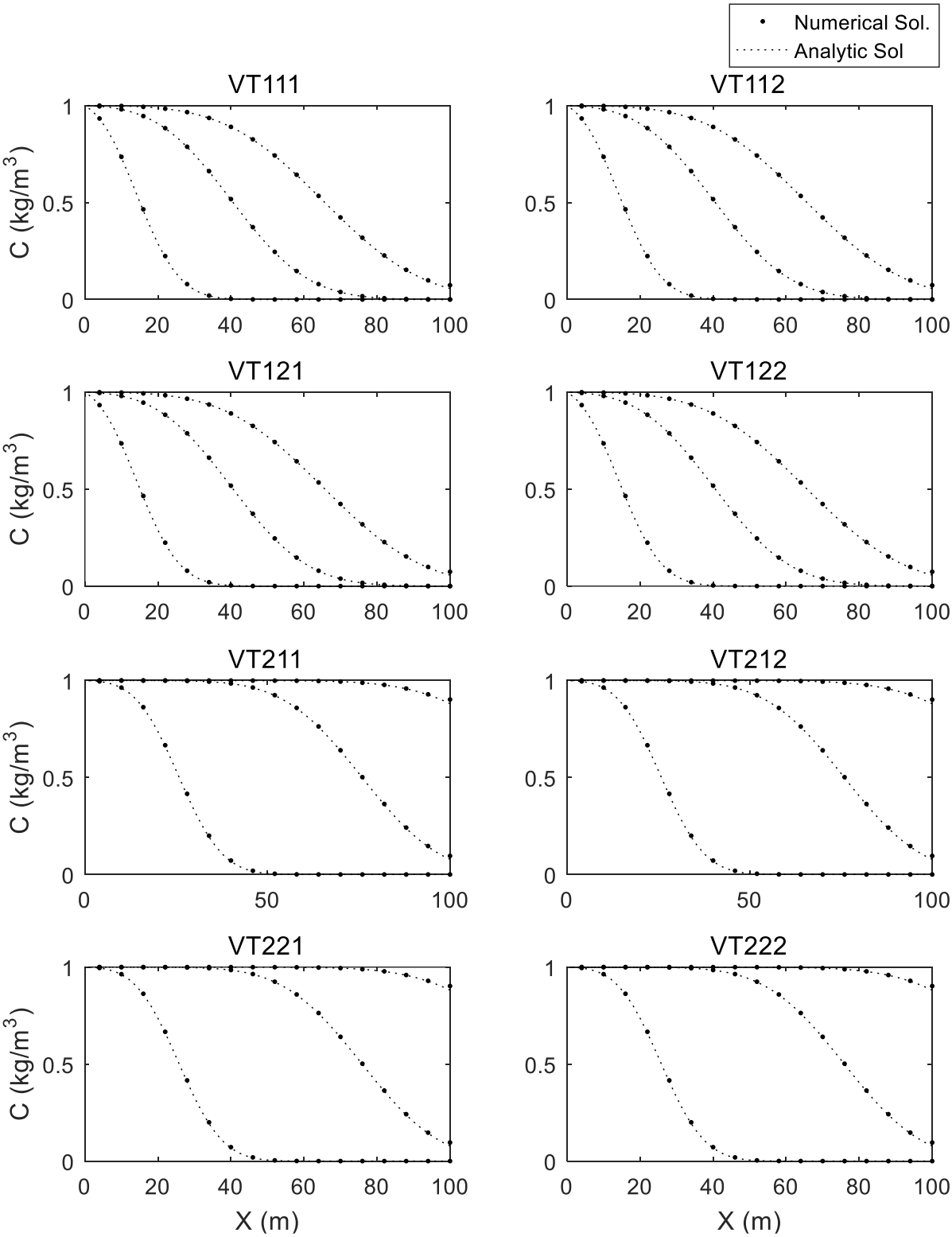
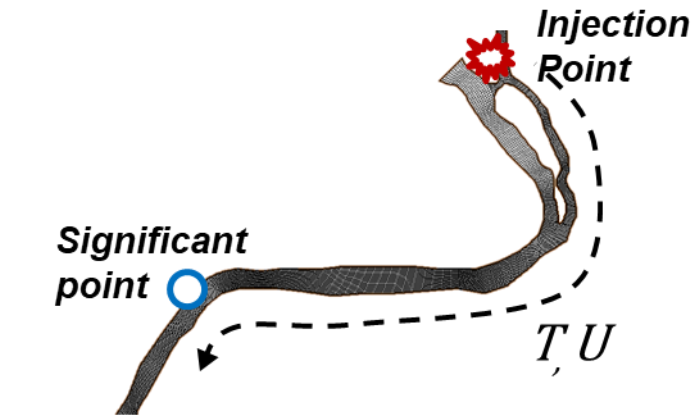


Figure 3.4 Validation results of volatilization (T = 2520 sec)

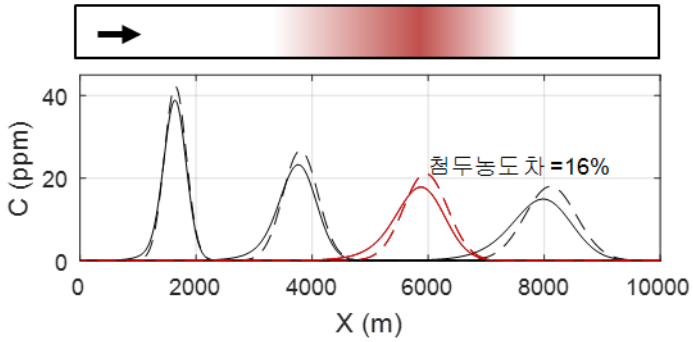
3.3 Algorithm for identifying significant reactions

When the pollutant spill accident occurs, the countermeasures should be established quickly in order to minimize the damage caused by it. For this purpose, this study proposes an algorithm to identify significant reaction in a target site to minimize computation time. For example, in the case of a hydrophilic material, only one (dissolved concentration) needs to be simulated out of three phases (dissolved concentration, particulate concentration on suspended sediment, and particulate concentration on riverbed). Then, calculation time can be reduced. However, if the discrimination of significance is wrong, the error can leads significant damages to us. Therefore, it is necessary to calculate an appropriate critical value for identifying the significance of the reaction term. In this study, we used the procedure shown in **Fig. 3.5** to derive dominant reaction process by parameters sensitivity analysis.

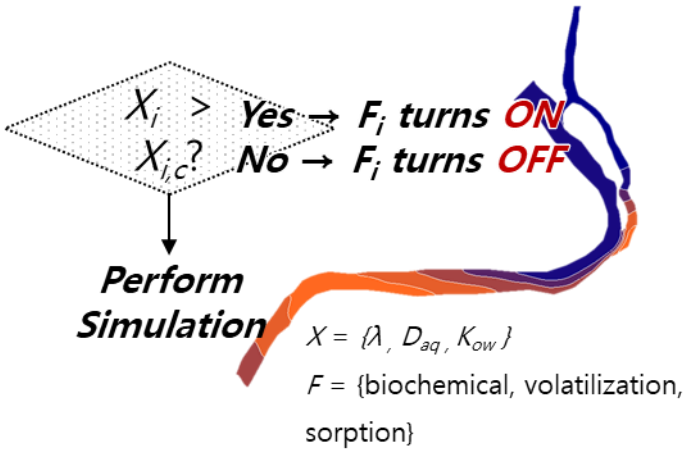
The steps of the Algorithm for identifying significant reactions is as followed. In first step, summarize the flow regime of the target site based on results of hydrodynamic simulation. In the accident response system of the NIER, the hydrodynamic simulation is automatically performed every day for 4 main rivers (Moon et al., 2012), so that it is assumed that hydro-topographic data are already built in the accident situations. In second step, construct the virtual rectangle channel, and perform the sensitivity analysis for the parameters of reaction terms. In nature streams, active reactions occur more than straight rectangle channel due to storage effect and secondary flow etc. Therefore, if the simulation is performed under the simplified condition, conservative threshold values can be obtained, and the time required for calculation can be reduced. For parameters for sensitivity analysis, water diffusion coefficient, biochemical reaction coefficient, and water - octanol partition coefficient were selected



1. Obtain average velocity and water depth, and distance from hydrodynamic model results



2. Discriminating significant mechanisms by sensitivity analysis



3. Perform simulation

Figure 3.5 Process to identify significance mechanisms

since another parameters are determined by the flow and topography conditions. Under the given condition in previous step, one-at-a-time sensitivity analysis is performed. The default parameter values are set to insignificant ones, and numerous simulation is conducted with updated parameter set that only one of the default parameter values is changed. If difference of the parameter value leads significant change of the simulation result, then the threshold value is determined as critical parameter for identifying significant reactions. The criteria for judging the significant change of simulation results were selected as the residence time and the peak concentration of pollutants which are needed to respond to the accident. In final step, the simulation is performed with only significant reaction terms.

4. Application

4.1 Study site

In this study, the study site was selected as the main stream of the Nakdong River in the area between the Gangjeong and Dalsung Weir. The Nakdong River is one of the major rivers in South Korea used as a water supply source in the southeastern region. The length of the river is 525 km and the drainage area is 23,817 km^2. There is tributary in the site, and the ratio of stream width to depth is 52.2 so that it can be considered as shallow water (Van Prooijen and Uijttewaal, 2005). Therefore, the depth-averaged two-dimensional model is effective in investigating the spatial variability of pollutants in the site

As shown in Figure 4.1, many industrial complexes exist at upstream of the site, and the agricultural complex is located on the middle and downstream sides of the site. It means the pollutant from industrial complex can directly effect on agricultural land. In addition, the flow rate is controlled by upstream and downstream at the weirs, and the flow rate is usually less than 100 cms. Low flow rates cause pollutants to remain, so the period of damages will be longer. Therefore, it is necessary to construct an incident response system that can predict the residence time at the main point of the pollutant and prepare measures for proper use water.

In order to apply the developed model in this study, the hydrodynamic simulation was performed by HDM-2D to obtain the flow velocity and depth of water.

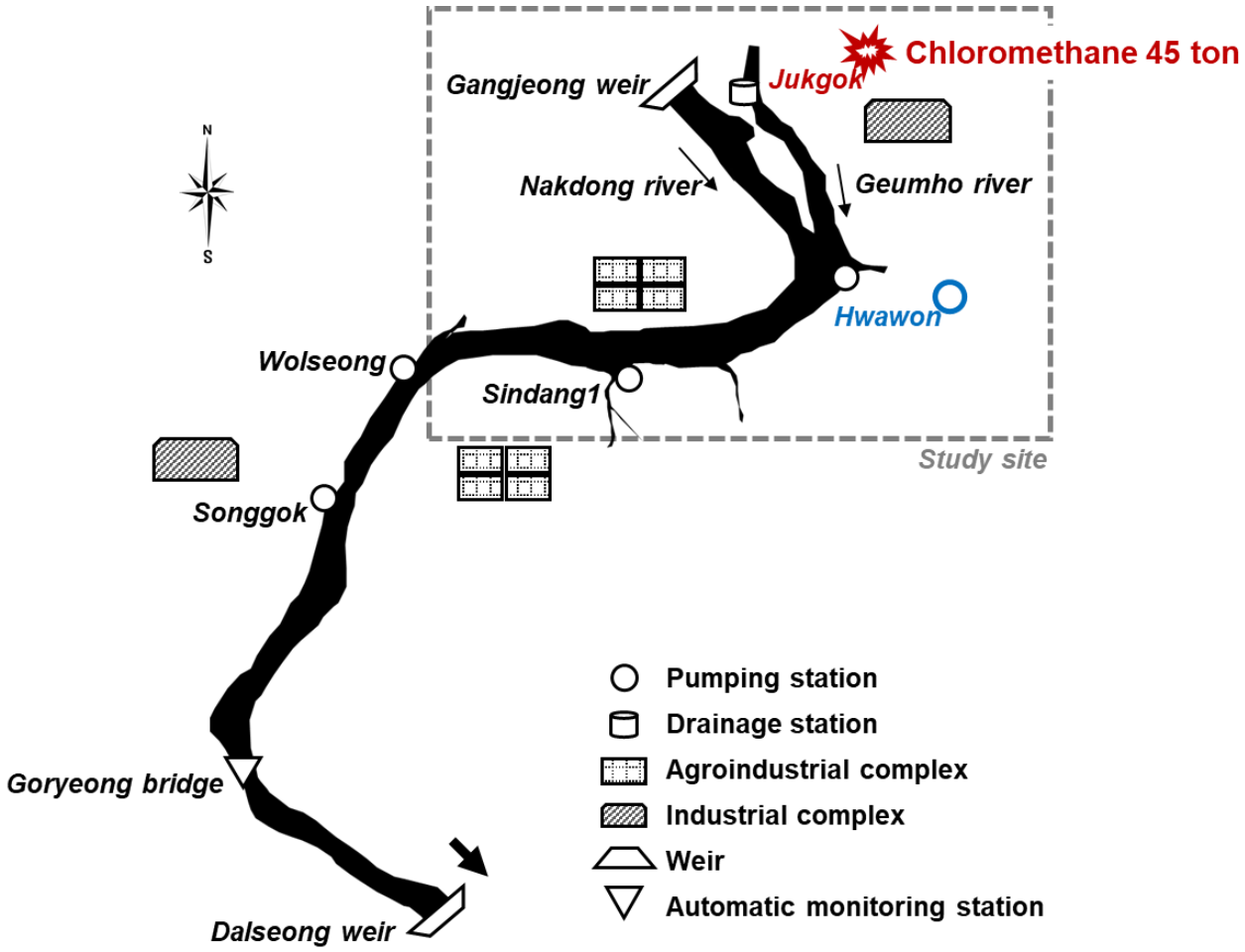
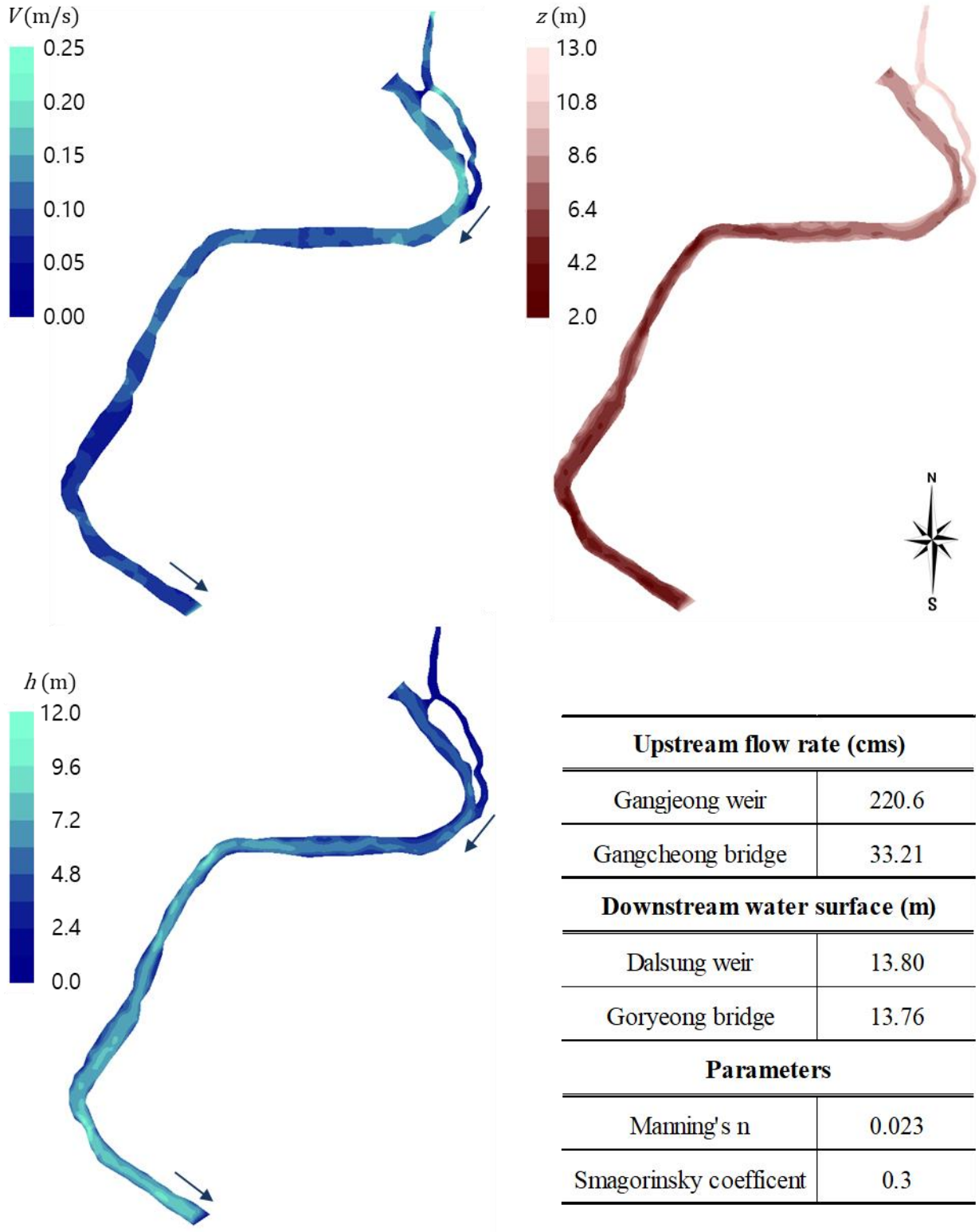


Figure 4.1 Location of study site and the facilities

The boundary conditions were set as the discharge amount and the upstream water level of the operation of Gangjeong-goryeong Weir and Dalsung Weir in the Water Management Information System (WAMIS) on May 9, 2018. The hydrodynamic simulation was conducted under steady-uniform flow condition since there were not significant change (see Appendix B). The Manning' n and Smagorinsky constants were set to 0.023 and 0.3, respectively, for calibration at the Gumi Bridge located downstream of the application area. **Fig. 4.2** shows the results and simulation conditions. The median value of the bed material diameter was 0.8 mm which is from Ryu et al. (2017). The median value of the suspended particle size was 0.042 mm d50 measured at the water quality monitoring station at upstream of the study site, and suspended transport simulation was performed using STM-2D to calculate the spatiotemporal distribution of suspended sediment concentration.



Upstream flow rate (cms)	
Gangjeong weir	220.6
Gangcheong bridge	33.21
Downstream water surface (m)	
Dalsung weir	13.80
Goryeong bridge	13.76
Parameters	
Manning's n	0.023
Smagorinsky coefficent	0.3

Figure 4.2 Hydrodynamic simulation results (HDM-2D) and the conditions

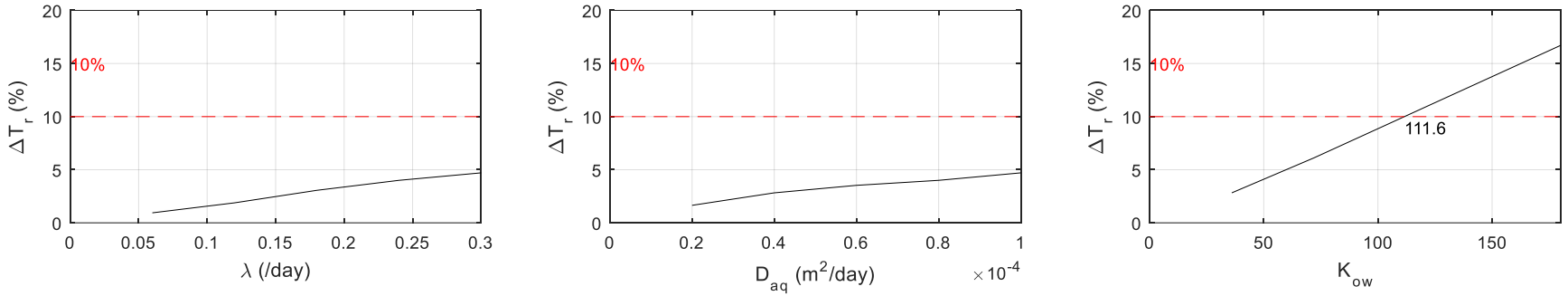
4.2 Critical values of reaction parameters

In order to apply the developed model, it is assumed that the accidental spill of toxic chemicals occurs in the Jung - gok drain at the confluence reach of Kumho River. The effects of pollutants on the Hwawon intake stations were investigated through numerical simulations. The simplified conditions for the sensitivity analysis are shown in **Table 4.1**. The distance from the Junggok to the Hwawon intake station is about 4 km, and the average flow rate is 0.108 m / s, and average depth is 2.1431 m. In CTM-2D, the longitudinal and transverse dispersion coefficients of the main stream were 8 m^2/s and 1 m^2/s, respectively. In the tributary, 3 m^2 / s and 0.1 m^2 / s were used. The parameters sensitivity were analyzed within the range of the characteristic values of 38 substances (see Appendix C) which are harmful chemical substances reported by the Ministry of Environment were responded to.

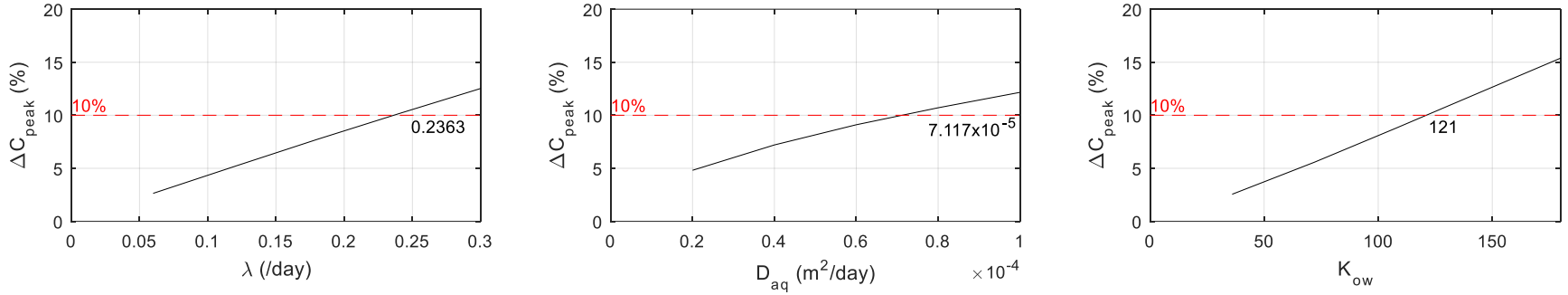
The sensitivity analysis results are shown in **Fig 4.3**. **Fig 4.3a** is the parameter value at which the peak concentration changes by 10%, and **Fig 4.3b** is the value when the retention time changes by more than 10%. Among the thresholds of the two criteria, a small value of the parameter was determined as the final critical value, 0.2363 / day for the biochemical reaction coefficient, 7.117x10-5 m^2/day for the water vapor diffusion coefficient, The partition coefficient of water - octanol was calculated as 111.5. Considering that the average flow rate is about 0.1 m / s and the residence time is 10 hours, the critical values were estimated relatively small than that of the material properties of the target 38 materials. Only two materials out of the 38 materials can be considered as conservative, and four materials can be considered as hydrophobic.

Table 4,1 Sensitivity analysis conditions to obtain critical values

Hydro conditions		**Sediment properties**	
velocity(U)	0.108 m/s	porosity (φ)	0.4
water depth(H)	2.1431 m	f_{oc}	0.0246
reach length	5 km	thickness of mixing layer (δ_m)	10 cm
dispersion coeffic	3 m2/s	concentration of SS (C_s)	10 ppm
grid size(dx)	25 m	**Material properties**	
time step(dt)	9 s	biochemical reaction coefficient (λ)	0~`27.36 m2/day
Pe	0.90	aqueous diffusion coefficient (D_{aq})	4.6e-5~1.3e-4 /day
Cr	0.04	partitioning coefficient (K_{ow})	3e-5~1059



(a) according to the change of the residence time



(b) according to the change of the peak concentration

Figure 4.3 Results of sensitivity analysis for each reaction parameters

4.3 Results

The toxicant transport was simulated based on the results of the determination of the significance of flow mechanism and reaction mechanism.The simulations were carried out with the parameters of methyl chloride which was determined as sensitive to sorption and volatilization process. Three simulation results were compared to evaluate the validity of the developed algorithm for identifying significance reaction process. The 3 cases are: 1) simulation results without reaction terms; 2) simulation results considering only significant reactions using the calculated critical values; and 3) simulation results reflecting all mechanisms. **Fig 4.4** shows the concentration-time graphs detected at the Hwawon intake station. When the first time the concentration was detected at the pumping station, it was from 6 hours after the accident and the main features are summarized in **Table 4.4**. **Fig 4.5** shows spatiotemporal distribution of concentration.

Case 1 and 2 showed about 100% change in peak concentration. Also, the residence time was about 33% with a difference of about 2 hours. In cases 2 and 3, the difference was 0.002 ppm in peak concentration and about 13 minutes in residence time, which are only about 3 %. When it comes to sorption mechanism, the shape is generally skewed by of the residence time increased. In this case, however, the residence time does not change significantly. After the dissolved contaminant was transferred, there was almost no contaminant remaining as adsorbed form.

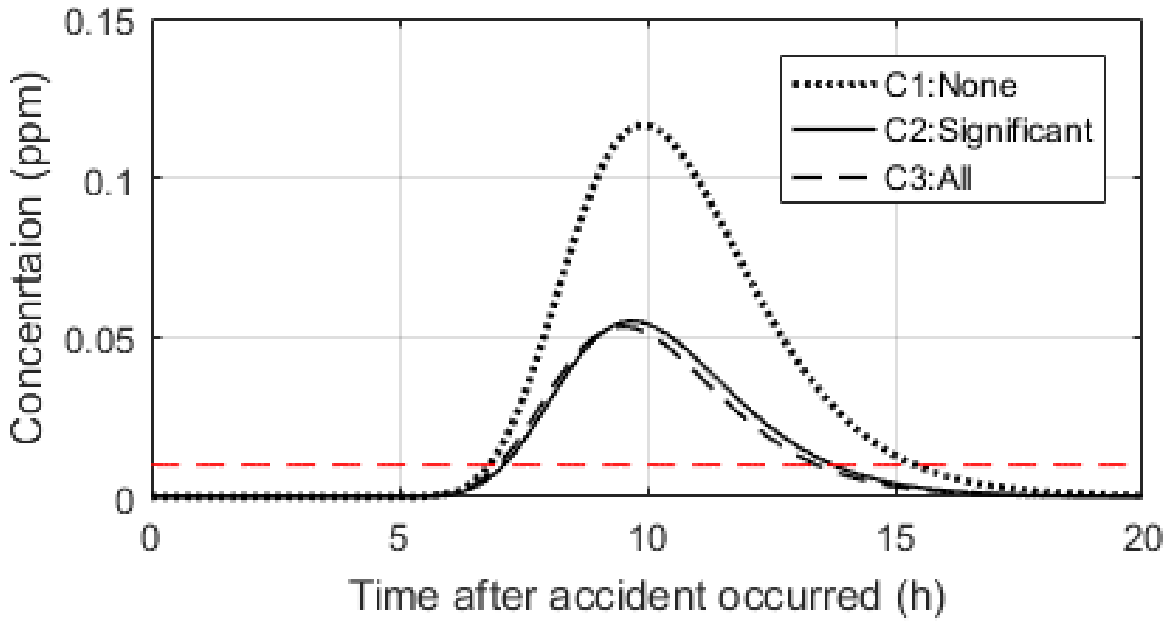


Figure 4.4 Concentration-time curve at Hwawon intake station

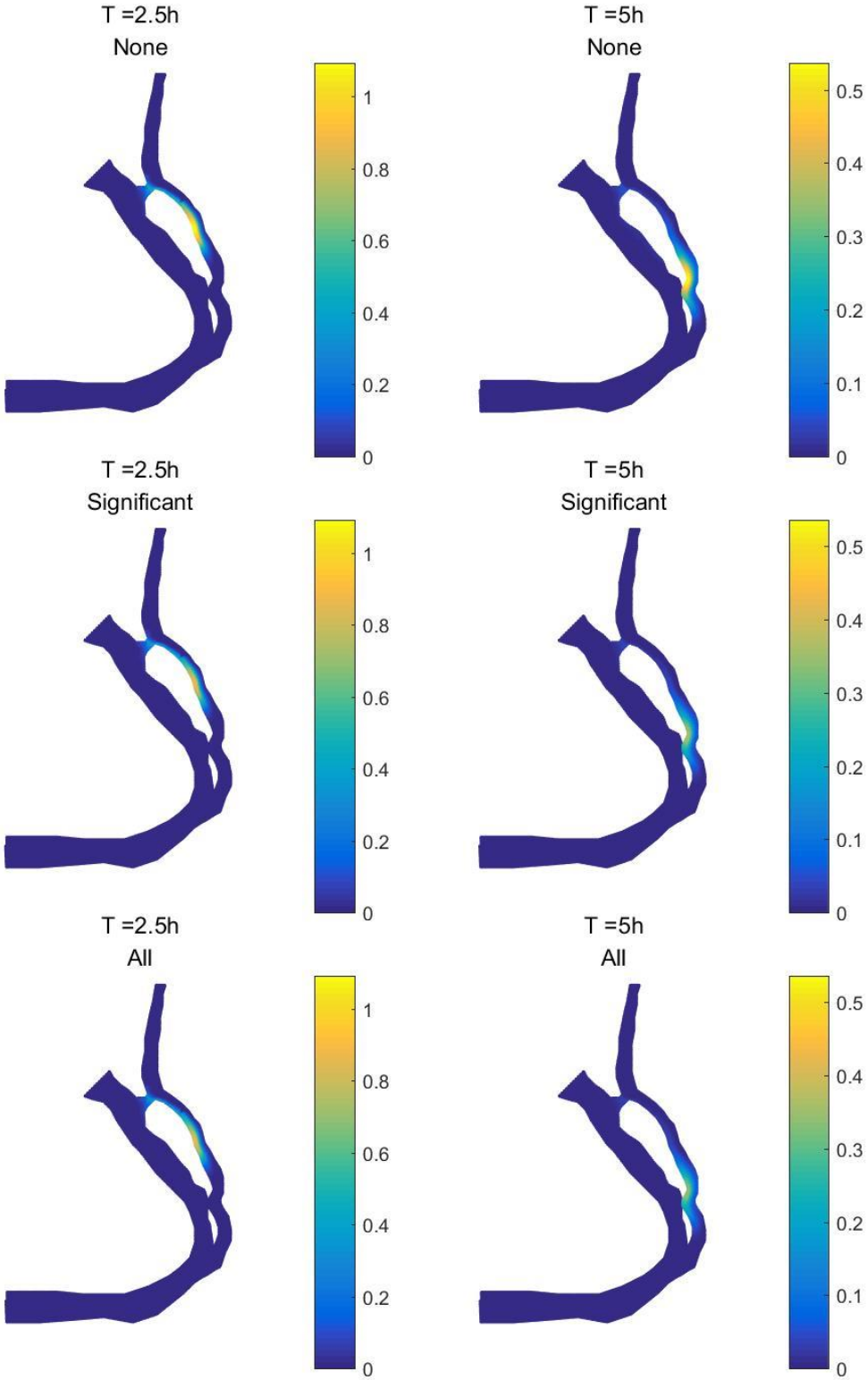


Figure 4.5 Results of model application

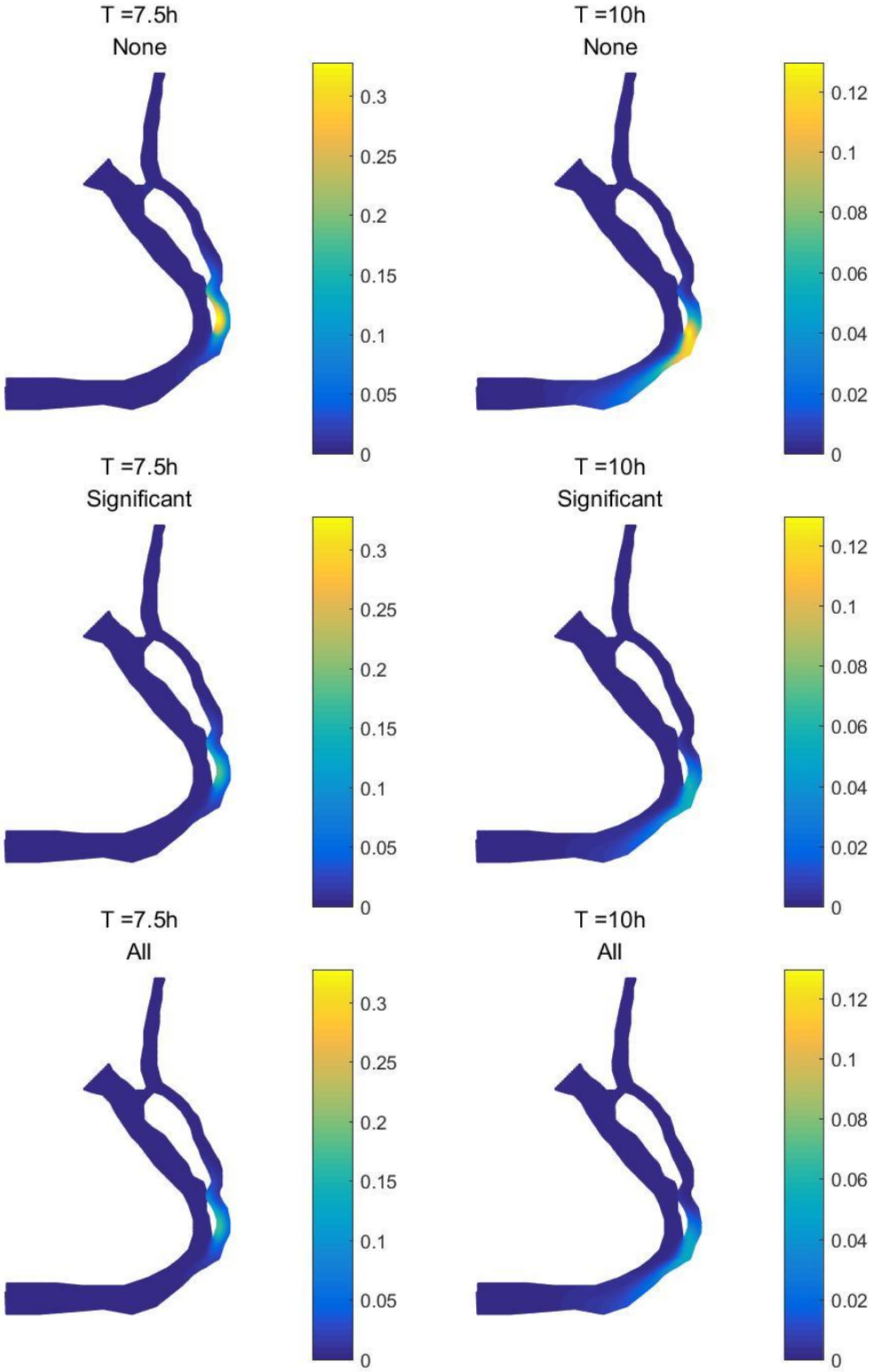


Figure 4.5 Results of model application (continued)

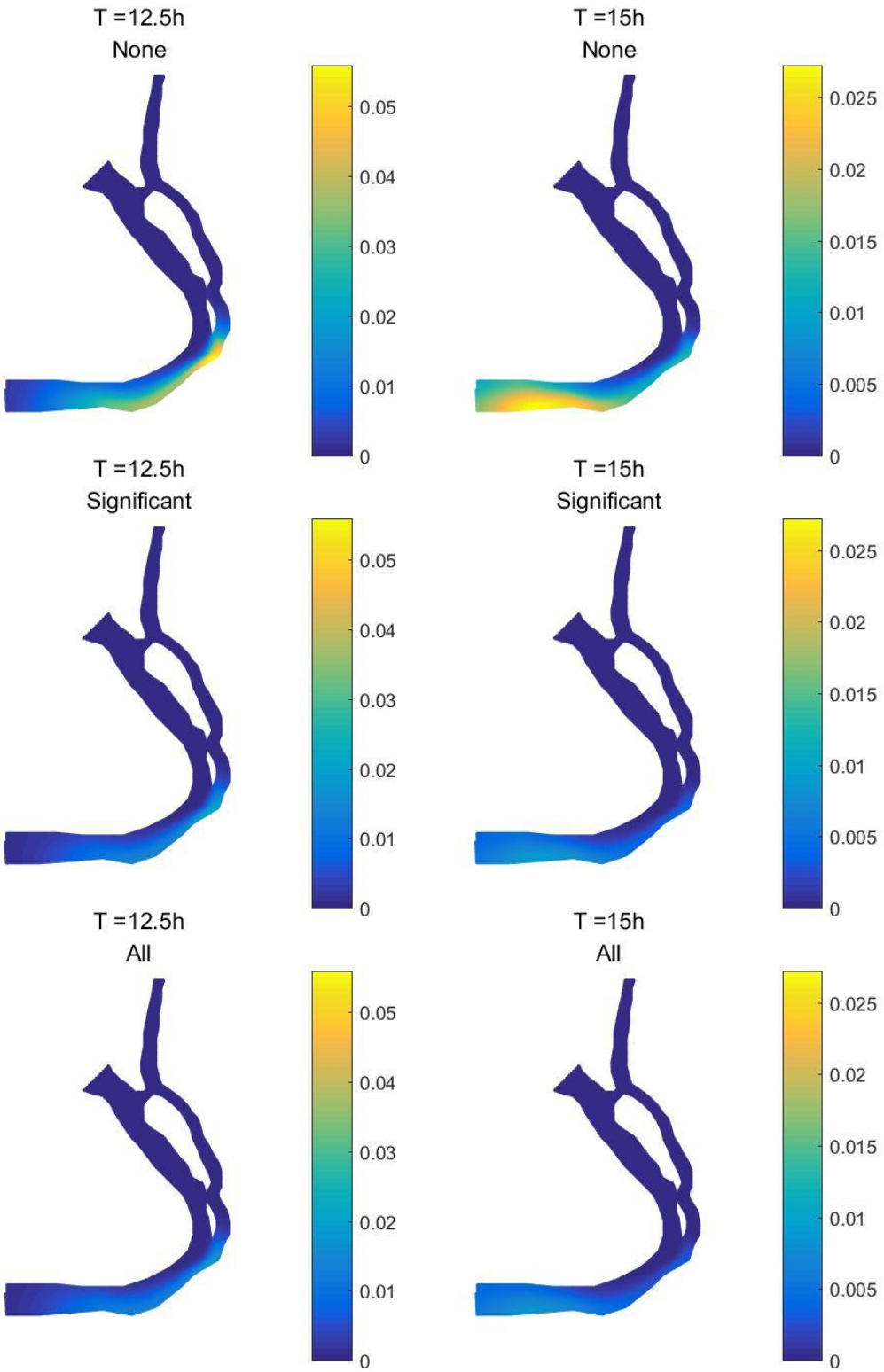


Figure 4.5 Results of model application

5. Conclusion

In this study, pollutant transport model for toxic chemicals was developed considering to be used in accident response system. The model can represent the reaction mechanisms of toxic chemical such as biochemical reactions, volatilization, and adsorption / desorption. These reactions were added to CTM-2D which is a two-dimensional water quality analysis model developed by Seoul National University. Each reaction mechanism is modelled as a first order reaction. Additionally, estimation equations of the reaction parameters were adopted in order to response to an accident immediately.

In order to estimate the water - soil partition coefficient, the water - octanol partition coefficient and the water - organic carbon partition coefficient regression equation proposed by Karickhoff (1981) were used. For the exchange rates of sorption, two estimation equations can be use selectively: Brusseau and Rao (1989) and Karickhoff and Morris (1985). For estimating the volatility coefficient, the equation proposed by Dobbins (1964) was used, and the biochemical reaction coefficients were from the literatures. The model was verified by comparing it with the analytic solution. The error was less than 0.1% which proved the validity of the model.

An algorithm for identifying significant reaction terms was proposed in order to operate the developed model efficiently. In order to cope with the accident quickly, the reduction of the computation time can be made by eliminating the insignificant terms according to the proposed algorithm. The developed model and algorithm were applied

to assess validity of the algorithm. The virtual accident was assumed as the toxic chemical inflows into the Kumho River where joins the Nakdong River. In order to examine applicability, three cases were compared taking into account the significant mechanism mentioned above ((1) results reflecting all reaction terms, (2) results reflecting only significant mechanisms, (3) results without reactions). In case of methyl chloride, the volatilization and biochemical reactions were identified as significant mechanisms while the sorption process was not. When comparing the case 2 and 3, the residence time at the Hwawon intake station was about 33% with about 2 hours difference. Also, in case of the peak concentration, there was 100% difference. When comparing the case 1 and 2, there was 3% changes in peak concentration and residual time which can be regarded as an acceptable difference considering the need for conservative judgment. The results showed that the algorithm for identifying significant reaction is valid in the given condition. Moreover, the calculation of case2 took only 1/4 times compared to case 1, and it is expected to provide a more appropriate countermeasure for the accidents.

Therefore, it is expected that the pollutant transport model for toxic chemicals and the algorithm for identifying the significant reaction mechanism in this study help to provide quicker decision for response to the river spill accidents.

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Korean Abstract

한국의 하천들은 하수처리시설과 취수시설이 혼재되어있어 수질오염사고가 발생할 가능성이 높다. 최근 신소재 공학 등 첨단산업이 발전하게 되면서 유해화학물질의 유입문제는 더욱 대두되고 있으며, 실제로 최근 유해화학물질 유입사고 발생건수가 늘어나고 있다. 또한 국내 취수량의 90%가 지표수에서 취수한다는 점을 고려하였을 때, 하천오염사고는 식수오염, 관개수 오염 등 형태의 즉각적인 피해로 이어지게 되므로 적절한 대응책이 필요하다. 특히 중-대하천에 유해화학물질이 유출되는 사고에 대해서는 주요지점(취수장, 친수지구 등)에 마다 그 특징에 따른 적절한 조치가 필요하다. 이러한 사고에 대비하여 환경부는 유해화학물질 유입사고대응체계를 구축하여 대응하고 있다. 본 연구에서는 이러한 대응체계에 탑재 가능한 FEM기반 2차원 유해화학물질의 거동 해석 모형을 개발하였으며, 개발된 모형의 효율적인 운영을 위한 반응항의 유의성 판별 알고리즘의 프레임을 제시하였다.

서울대학교에서 개발한 2차원 수질해석 모형인 CTM-2D를 기반으로 생화학적반응, 휘발 그리고 흡탈착 메커니즘을 고려한 유해화학물질 해석 모형을 개발하였다. 각 반응 메커니즘은 1차 반응항으로 구성되며 사고에 즉각적으로 대비하기 위해 각 메커니즘의 매개변수들을 구축된 DB를 통해 추정할 수 있도록 여러가지 추정식을 탑재하였다. 물-토양 분배계수를 추정하기 위하여 Karickhoff (1981)가 제안한 물-옥탄올 분배계수와 물-유기탄소 분배계수 회귀식을 사용하였으며, 휘발계수를 추정하기 위해 Dobbins (1964)의 회귀식을 사용하였으며, 생화학적 반응계수는 문헌들의 값을 사용하였다. 구축된 반응항들을 검증하기 위해 해석해와 모형의 결과값을 비교하였으며, 0.1% 미만의 오차를 보여 모형의 타당성이

입증되었다.

또한 개발된 모형을 효율적으로 운영하기 위해 각 입력변수의 민감도 분석을 사용한 유의성 판별 알고리즘을 제시하고, 이를 이용해 유의하지 않은 항을 제거하여 계산소요시간이 단축할 수 있도록 하였다. 본 알고리즘의 첫째 과정은 미리 업데이트된 수리모형의 결과 값을 이용하여 유입지점으로부터 주입지점까지의 유하거리 및 평균 유속 그리고 평균 수심을 산정한다. 그 다음 구축된 지형 특성 자료를 이용해 단순화된 가상 직사각수로를 구축하고, 반응항의 매개변수를 유의하지 않은 값을 시작으로 매개변수의 값을 올려가며 결과에 유의한 변화를 가져오는 임계 값을 산정한다. 그 다음 구해진 임계 값과 실제 유입된 물질의 매개변수를 비교하여 유의한 메커니즘을 판별하고 모의를 수행하게 된다.

개발된 모형과 유의성 판별 알고리즘을 낙동강 중상류에 있는 낙동고령보와 달성보 사이의 금호강 합류부 구간의 가상 유해화학물질 유입사고를 가정하여 적용하고, 그 결과를 분석함으로 적용성을 검토하였다. 금호강 합류부의 죽곡 배수장에서 사고가 발생하여 톨루엔이 유출되었다고 가정하여, 4 km 유하거리 낙동강 합류지점에 있는 화원 양수장을 주요지점으로 설정해 모의를 수행하였다. 수리모의를 위해 첨단기술 기반 하천 운영 및 관리 선진화 연구단에서 2016년에 측량한 하상자료가 사용되었으며, 국가수자원관리 종합정보시스템(WAMIS)의 유황자료를 사용하였다. 또한 유의성 판별 알고리즘의 적용성 검토를 위해 3가지 조건으로 모의를 진행하였다.

적용성 검토를 위해 앞서 언급한 유의한 반응항만 고려한 모의를 포함해 총 3가지 케이스를 비교하였다((1)모든 반응항이 미반영된 결과, (2)유의한 메커니즘만 반영된 결과, (3)모든 메커니즘이 반영된 결과). 사고대비 물질 38종 중 휘발 및 생화학반응이 유의하게 판별된 염화메틸

물질을 대상으로 모의를 진행하였으며, 모든 메커니즘을 반영하지 않은 결과와 유의한 메커니즘을 반영한 결과 는 첨두농도에서 약 100 %의 변화를 보였고, 체류시간은 약 2시간 정도의 차이로 약 33 % 변화를 보였다. 이는 사고 시 대처 방안에 고려해야 할 차이로 볼 수 있다. 또한 유의한 메커니즘만 반영한 결과와 유의하지 않은 메커니즘까지 모두 반영한 결과를 비교하였을 때 첨두농도에서 0.002 ppm 차이, 체류시간에서는 약 13분 가량의 차이를 보였으며, 이는 유의한 메커니즘만 반영한 결과 대비 약 3 % 정도의 변화를 보였으며, 사고 대응책은 보수적인 판단이 필요함을 고려하였을 때, 허용 가능한 차이로 볼 수 있다. 따라서 이는 주어진 조건의 시나리오 상황에서 제시된 유의성 판별이 타당함을 보였다. 또한 계산소요시간이 1/4로 줄어들어 신속한 대응책이 필요한 하천유입사고발생 시 보다 적절한 대응책을 마련할 수 있을 것으로 기대된다.

따라서 하천에 유해화학물질 유입사고가 일어날 시 본 연구에서 개발한 유해화학물질 거동해석모형과 제시한 유의성 판별 알고리즘을 이용해 보다 신속한 대비가 가능할 것으로 기대된다.

Keywords: 하천오염사고, 사고대응체계, 2차원 수치모형, 독성물질 거동해석모형, 유의반응판별 알고리즘.

Appendix A. Mixing layer

The mixing layer refers to a layer in which sediment erosion occurs. In the layer, Wu (2007) observed that dissolved contaminants exchange occurs due to adsorption / desorption between waterbody and riverbed. Karim and Kennedy (1982) found that the thickness of the mixed layer is 0.1 to 0.2 times the depth of the water, and Borah et al. (1982):

$$\delta_m = \frac{d_L}{(1 - p'_m)p_{bm}} \quad \textbf{(A.1)}$$

where d_L is the smallest particle size of the immobile bed material; p_{bm} is the ratio of moving bed material in the mixing layer. In addition, Niekerk et al. (1992) proposed the relationship between the dimensionless shear stress and the dimensionless stress as follows.

$$\delta_{\mathrm{m}} = 2d_{50}\frac{\tau'_b}{\tau_{c50}} \quad \textbf{(A.2)}$$

where d_{50} is the median of bed material; τ_b' s the friction factor of the bed shear stress; τ_{c50} is the initial kinetic critical shear stress for the d_{50} bed material. Wu and Vieira (2002) also proposed a estimation of thickness of mixing layer as follow using the height of dune and d_{50}.

$$\delta_m = \max[0.5\Delta, 2d_{50}] \tag{A.3}$$

where Δ is the height of the dune, and van Rijn (1984) proposed the following equation.

$$\Delta = 0.11h\left(\frac{d_{50}}{h}\right)^{0.3}(1-\exp(-0.5T))(25-T) \tag{A.4}$$

$$T = \frac{(u_*')^2 - \left(u_{*,cr}\right)^2}{\left(u_{*,cr}\right)^2} \tag{A.5}$$

where u_*'(= ($g^{0.5}$/C') $\bar{u}$) is the bottom shear velocity of the particles; C'(= *18 log*((*12*R_b) / (*3*D_{90}))) is the Chezy constant of particles; R_b is the hydraulic radius propseed by Vanoni-Brooks, $\bar{u}$ is the mean velocity; $u_{*,cr}$ is the critical shear rate proposed by Shields.

Appendix B – Flow conditions of study site

Time	Gangjeong weir	Dalsung weir	Goryeong bridge		Gangchang bridge
	flow rate	water level	water level	water level	flow rate
	(㎥/s)	(El.m)	(El.m)	(El.m)	(㎥/s)
20180521 01	312.9	13.82	3.19	13.79	33.21
20180521 02	243.7	13.82	3.16	13.76	33.21
20180521 03	220.6	13.78	3.14	13.74	33.21
20180521 04	220.6	13.78	3.14	13.74	33.21
20180521 05	220.6	13.77	3.14	13.74	33.21
20180521 06	220.6	13.79	3.15	13.75	33.21
20180521 07	220.7	13.80	3.16	13.76	33.21
20180521 08	220.6	13.80	3.16	13.76	33.21
20180521 09	220.6	13.81	3.17	13.77	33.21
20180521 10	220.7	13.82	3.18	13.78	33.21
20180521 11	220.6	13.80	3.16	13.76	33.21
20180521 12	220.6	13.79	3.15	13.75	33.21
20180521 13	220.6	13.78	3.14	13.74	33.21
20180521 14	220.5	13.77	3.14	13.74	33.21
20180521 15	220.6	13.77	3.13	13.73	33.21
20180521 16	220.6	13.79	3.15	13.75	33.21
20180521 17	222.9	13.79	3.16	13.76	33.21
20180521 18	222.3	13.81	3.17	13.77	33.21
20180521 19	220.9	13.82	3.18	13.78	33.21
20180521 20	221.0	13.82	3.18	13.78	33.21
20180521 21	220.7	13.81	3.18	13.78	33.21
20180521 22	220.7	13.82	3.18	13.78	33.21
20180521 23	220.9	13.82	3.18	13.78	33.21
20180521 24	221.1	13.82	3.18	13.78	33.21

Appendix C. List of Accidental materials

	Name	log K_{ow}	D_{aq} [m^2/day]	λ [/day]
1	2-Choloroethanol	0.03	1.0.E−04	2.4.E−02
2	2-Cloroethydiethyl ammonium chloride	−1	−	4.1.E−08
3	Acrolein	−0.01	1.0.E−04	3.8.E+00
4	Amiton	2.925	4.6.E−05	4.8.E−06
5	Ammonia	−1.38	−	1.0.E−01
6	Ammonium bifluoride	−4.37	−	7.4.E−07
7	Arsenic trichloride	1.61	−	5.0.E−01
8	Bromine	1.26	8.9.E−05	1.3.E+01
9	Chlorine	1.2	9.3.E−05	1.9.E+01
10	Chloropicrin	1.32	7.9.E−05	9.9.E+00
11	Cyanogen chloride	0.07	1.0.E−04	2.0.E+01
12	Ethylene oxide	−0.3	1.2.E−04	5.0.E+00
13	Hydrogen chloride	0.54	−	2.5.E+01
14	Hydrogen cyanide	−0.25	1.3.E−04	5.9.E+00
15	Hydrogen fluoride	0.23	−	2.1.E−09
16	Hydrogen selenide	0.24	−	1.7.E+01
17	Mechlorethamine	0.91	6.5.E−05	6.6.E−02
18	Methyl bromide	1.19	1.1.E−04	1.6.E+01
19	Methyl chlorine	0.91	1.1.E−04	2.2.E+01
20	Methyl ethyl ketone	0.29	8.5.E−05	1.7.E+00
21	Methyl isocynate	0.37125	1.1.E−04	1.3.E+01
22	Mustard gas	2.38	6.9.E−05	5.3.E−01
23	Paraquat	−4.5	−	5.7.E−09
24	Phosgene	0.03	1.0.E−04	1.6.E+01
25	Phosphine	−0.27	−	2.7.E+01
26	Phosphorus oxychloride	0.95	8.3.E−05	2.0.E−01
27	Phosphorus pentachloride	−3.47	−	4.6.E−01
28	Phosphorus pentasulfide	−0.46	−	1.1.E+01
29	Phosphorus trichloride	1.815	8.5.E−05	5.6.E+00
30	Potassium cyanide	−1.69	−	5.5.E−16
31	Potassium fluoride	−0.77	−	2.5.E−18
32	Sarin	0.3	6.6.E−05	1.4.E−02
33	Sodium cyanide	−1.69	−	4.9.E−15
34	Sodium fluoride	−0.77	−	2.2.E−28
35	Sulfur monochloride	3.025	7.7.E−05	1.4.E+01
36	Sulfuric acid	−2.67	1.2.E−04	7.3.E−07
37	Thionyl chloride	0.89	8.2.E−05	6.4.E−02
38	Toluene	2.73	7.6.E−05	1.6.E+01

* : significant mechanisms